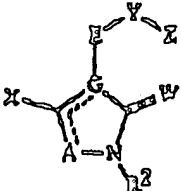




INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C07D 249/12, A01N 43/653, C07D 403/12, A01N 43/66, 43/707	A1	(11) International Publication Number: WO 98/20003 (43) International Publication Date: 14 May 1998 (14.05.98)
(21) International Application Number: PCT/US97/17608 (22) International Filing Date: 1 October 1997 (01.10.97) (30) Priority Data: 60/029,965 1 November 1996 (01.11.96) US (71) Applicant (for all designated States except US): E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US). (72) Inventor; and (75) Inventor/Applicant (for US only): WALKER, Michael, Paul [US/US]; 22 Matthews Road, Newark, DE 19713 (US). (74) Agent: HEISER, David, E.; E.I. du Pont de Nemours and Company, Legal Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).		(81) Designated States: AL, AM, AU, AZ, BA, BB, BG, BR, BY, CA, CN, CU, CZ, EE, GE, HU, ID, IL, IS, JP, KG, KP, KR, KZ, LC, LK, LR, LT, LV, MD, MG, MK, MN, MX, NO, NZ, PL, RO, RU, SG, SI, SK, SL, TJ, TM, TR, TT, UA, US, UZ, VN, YU, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: FUNGICIDAL CYCLIC AMIDES <div style="text-align: center;">  <div style="margin-left: 20px;">(I)</div> </div> (57) Abstract <p>Compounds of formula (I), and their N-oxides and agriculturally suitable salts, are disclosed which are useful as fungicides wherein E is 1,2-phenylene optionally substituted with R³ or both R³ and R⁴; A is O, S, N, NR⁵ or CR⁶; G is C or N; provided that when G is C, then A is O, S or NR⁵ and the floating double bond is attached to G; and when G is N, then A is N or CR⁶ and the floating double bond is attached to A; W is O, S, NH, N(C₁-C₆ alkyl) or NO(C₁-C₆ alkyl); X is OR¹, S(O)_mR¹ or halogen; Y is -O-, -S(O)_n-, -NR⁷-, -CH₂O-, -CH₂NR⁷-, -CH₂S(O)_n- or a direct bond; and the directionality of the Y linkage is defined such that the moiety depicted on the left side of the linkage is bonded to E and the moiety on the right side of the linkage is bonded to Z; Z is phenyl, pyrimidinyl or triazinyl, each substituted with R⁹ and optionally substituted with one or more R¹⁰; R² is H, C₁-C₆ alkyl, C₁-C₆ haloalkyl, C₂-C₆ alkenyl, C₂-C₆ haloalkenyl, C₂-C₆ alkynyl, C₂-C₆ haloalkynyl, C₃-C₆ cycloalkyl, C₂-C₄ alkylcarbonyl, C₂-C₄ alkoxycarbonyl, hydroxy, C₁-C₂ alkoxy or acetyloxy. Also disclosed are compositions containing the compounds of formula (I) and a method for controlling plant diseases caused by fungal plant pathogens which involves applying an effective amount of a compound of formula (I).</p>		

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TITLE

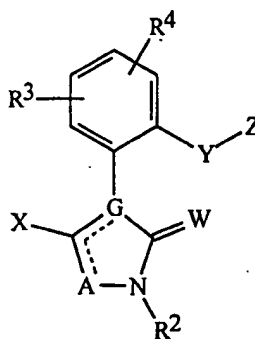
FUNGICIDAL CYCLIC AMIDES

BACKGROUND OF THE INVENTION

This invention relates to certain fungicidal cyclic amides their *N*-oxides,
 5 agriculturally suitable salts and compositions, and methods of their use as fungicides.

The control of plant diseases caused by fungal plant pathogens is extremely
 important in achieving high crop efficiency. Plant disease damage to ornamental,
 vegetable, field, cereal, and fruit crops can cause significant reduction in productivity
 and thereby result in increased costs to the consumer. Many products are commercially
 10 available for these purposes, but the need continues for new compounds which are more
 effective, less costly, less toxic, environmentally safer or have different modes of action.

International Publications WO 95/14009 and WO 97/00612 disclose cyclic amides
 of Formula i as fungicides and/or insecticides:

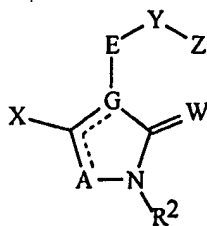


i

15 Compounds of the present invention are unexpectedly more effective as
 fungicides than those named in International Publications WO 95/14009 and
 WO 97/00612.

SUMMARY OF THE INVENTION

This invention is directed to compounds of Formula I including all geometric and
 20 stereoisomers, *N*-oxides, and agriculturally suitable salts thereof, agricultural
 compositions containing them and their use as fungicides:



I

wherein

25 E is 1,2-phenylene optionally substituted with R³ or both R³ and R⁴;

- A is O, S, N, NR⁵ or CR⁶;
- G is C or N; provided that when G is C, then A is O, S or NR⁵ and the floating double bond is attached to G; and when G is N, then A is N or CR⁶ and the floating double bond is attached to A;
- 5 W is O, S, NH, N(C₁-C₆ alkyl) or NO(C₁-C₆ alkyl);
- X is OR¹, S(O)_mR¹ or halogen;
- R¹ is C₁-C₆ alkyl, C₁-C₆ haloalkyl, C₂-C₆ alkenyl, C₂-C₆ haloalkenyl, C₂-C₆ alkynyl, C₂-C₆ haloalkynyl, C₃-C₆ cycloalkyl, C₂-C₄ alkylcarbonyl or C₂-C₄ alkoxycarbonyl;
- 10 R² is H, C₁-C₆ alkyl, C₁-C₆ haloalkyl, C₂-C₆ alkenyl, C₂-C₆ haloalkenyl, C₂-C₆ alkynyl, C₂-C₆ haloalkynyl, C₃-C₆ cycloalkyl, C₂-C₄ alkylcarbonyl, C₂-C₄ alkoxycarbonyl, hydroxy, C₁-C₂ alkoxy or acetyloxy;
- R³ and R⁴ are each independently halogen, cyano, nitro, hydroxy, C₁-C₆ alkyl, C₁-C₆ haloalkyl, C₂-C₆ alkenyl, C₂-C₆ haloalkenyl, C₂-C₆ alkynyl, C₂-C₆ haloalkynyl, C₁-C₆ alkoxy, C₁-C₆ haloalkoxy, C₂-C₆ alkenyloxy, C₂-C₆ alkynyloxy, C₁-C₆ alkylthio, C₁-C₆ alkylsulfinyl, C₁-C₆ alkylsulfonyl, formyl, C₂-C₆ alkylcarbonyl, C₂-C₆ alkoxycarbonyl, NH₂C(O), (C₁-C₄ alkyl)NHC(O), (C₁-C₄ alkyl)₂NC(O), (R¹³)₃Si, (R¹³)₃Ge, (R¹³)₃Si-C≡C, phenyl, phenylethynyl, benzoyl or phenylsulfonyl, each phenyl, phenylethynyl, benzoyl and phenylsulfonyl substituted with R⁸ and optionally substituted with one or more R¹⁰; or
- 15 when R³ and R⁴ are attached to adjacent atoms, R³ and R⁴ can be taken together as C₃-C₅ alkylene, C₃-C₅ haloalkylene, C₃-C₅ alkenylene or C₃-C₅ haloalkenylene, each optionally substituted with 1-2 C₁-C₃ alkyl;
- 20 R⁵ is H, C₁-C₆ alkyl, C₁-C₆ haloalkyl, C₂-C₆ alkenyl, C₂-C₆ haloalkenyl, C₂-C₆ alkynyl, C₂-C₆ haloalkynyl, C₃-C₆ cycloalkyl, C₂-C₄ alkylcarbonyl or C₂-C₄ alkoxycarbonyl;
- Y is -O-, -S(O)_n-, -NR⁷-, -CH₂O-, -CH₂NR⁷-, -CH₂S(O)_n- or a direct bond; and the directionality of the Y linkage is defined such that the moiety depicted on the left side of the linkage is bonded to E and the moiety on the right side of the linkage is bonded to Z;
- 30 Z is phenyl, pyrimidinyl or triazinyl, each substituted with R⁹ and optionally substituted with one or more R¹⁰;
- R⁶ is H, halogen, C₁-C₆ alkyl, C₁-C₆ haloalkyl, C₂-C₆ alkenyl, C₂-C₆ haloalkenyl, C₂-C₆ alkynyl, C₂-C₆ haloalkynyl or C₃-C₆ cycloalkyl;
- 35 R⁷ is H, C₁-C₃ alkyl or C₃-C₆ cycloalkyl; or R⁷ is phenyl or benzyl, each optionally substituted on the phenyl ring with halogen, C₁-C₄ alkyl, C₁-C₄ haloalkyl, C₁-C₄ alkoxy, C₁-C₄ haloalkoxy, nitro or cyano;

- R^8 is H, 1-2 halogen, C_1 - C_6 alkyl, C_1 - C_6 haloalkyl, C_1 - C_6 alkoxy,
 C_1 - C_6 haloalkoxy, C_2 - C_6 alkenyl, C_2 - C_6 haloalkenyl, C_2 - C_6 alkynyl,
 C_1 - C_6 alkylthio, C_1 - C_6 haloalkylthio, C_1 - C_6 alkylsulfinyl,
 C_1 - C_6 alkylsulfonyl, C_3 - C_6 cycloalkyl, C_3 - C_6 alkenyloxy,
 $CO_2(C_1$ - C_6 alkyl), $NH(C_1$ - C_6 alkyl), $N(C_1$ - C_6 alkyl) $_2$, cyano, nitro,
 $SiR^{14}R^{15}R^{16}$ or $GeR^{14}R^{15}R^{16}$;
- R^9 is phenyl, phenylmethyl, phenoxy, benzoyl, pyridinyl, pyridinyloxy, thienyl,
 thienyloxy, furanyl, pyrimidinyl or pyrimidinyloxy, each substituted on the
 aromatic ring with one or more R^{11} and with one R^{12} ;
- each R^{10} is independently halogen, C_1 - C_4 alkyl, C_1 - C_4 haloalkyl, C_2 - C_4 alkenyl,
 C_2 - C_4 alkynyl, C_1 - C_4 alkoxy, nitro or cyano;
- each R^{11} is independently halogen, cyano, nitro, C_1 - C_4 alkyl, C_1 - C_4 haloalkyl,
 C_2 - C_6 alkenyl, C_2 - C_6 alkynyl, C_1 - C_4 alkoxy, C_1 - C_4 alkylthio,
 C_1 - C_4 alkylsulfinyl or C_1 - C_4 alkylsulfonyl;
- R^{12} is halogen, C_1 - C_4 alkyl, C_1 - C_4 haloalkyl, C_2 - C_6 alkenyl, C_2 - C_6 haloalkenyl,
 C_2 - C_6 alkynyl, C_2 - C_6 haloalkynyl, C_2 - C_6 alkoxyalkyl, C_2 - C_6
 alkylthioalkyl, C_3 - C_6 alkoxyalkynyl, C_7 - C_{10} tetrahydropyranyloxyalkynyl,
 benzyloxymethyl, C_1 - C_4 alkoxy, C_1 - C_4 haloalkoxy, C_3 - C_6 alkenyloxy,
 C_3 - C_6 haloalkenyloxy, C_3 - C_6 alkynyloxy, C_3 - C_6 haloalkynyloxy, C_2 - C_6
 alkoxyalkoxy, C_5 - C_9 trialkylsilylalkoxyalkoxy, C_2 - C_6 alkylthioalkoxy,
 C_1 - C_4 alkylthio, C_1 - C_4 haloalkylthio, C_1 - C_4 alkylsulfinyl, C_1 - C_4
 haloalkylsulfinyl, C_1 - C_4 alkylsulfonyl, C_1 - C_4 haloalkylsulfonyl, C_3 - C_6
 alkenylthio, C_3 - C_6 haloalkenylthio, C_2 - C_6 alkylthioalkylthio, nitro, cyano,
 thiocyanato, hydroxy, $N(R^{17})_2$, SF_5 , $Si(R^{13})_3$, $Ge(R^{13})_3$, $(R^{13})_3Si-C\equiv C-$,
 $OSi(R^{13})_3$, $OGe(R^{13})_3$, $C(=O)R^{17}$, $C(=S)R^{17}$, $C(=O)OR^{17}$, $C(=S)OR^{17}$,
 $C(=O)SR^{17}$, $C(=S)SR^{17}$, $C(=O)N(R^{17})_2$, $C(=S)N(R^{17})_2$, $OC(=O)R^{17}$,
 $OC(=S)R^{17}$, $SC(=O)R^{17}$, $SC(=S)R^{17}$, $N(R^{17})C(=O)R^{17}$, $N(R^{17})C(=S)R^{17}$,
 $OC(=O)OR^{18}$, $OC(=O)SR^{18}$, $OC(=O)N(R^{17})_2$, $SC(=O)OR^{18}$, $SC(=O)SR^{18}$,
 $S(O)_2OR^{17}$, $S(O)_2N(R^{17})_2$, $OS(O)_2R^{18}$ or $N(R^{17})S(O)_2R^{18}$; or R^{12} is
 phenyl, phenoxy, benzyl, benzyloxy, phenylsulfonyl, phenylethynyl or
 pyridinylethynyl, each optionally substituted on the aromatic ring with
 halogen, C_1 - C_4 alkyl, C_1 - C_4 haloalkyl, C_1 - C_4 alkoxy, C_1 - C_4 haloalkoxy,
 nitro or cyano;
- each R^{13} is independently C_1 - C_4 alkyl, C_1 - C_4 haloalkyl, C_2 - C_4 alkenyl,
 C_1 - C_4 alkoxy or phenyl;
- R^{14} , R^{15} , and R^{16} are each independently C_1 - C_6 alkyl, C_2 - C_6 alkenyl,
 C_1 - C_4 alkoxy or phenyl;

each R¹⁷ is independently H, C₁-C₆ alkyl, C₁-C₆ haloalkyl, C₂-C₆ alkenyl, C₂-C₆ haloalkenyl, C₂-C₆ alkynyl, C₂-C₆ haloalkynyl, C₃-C₆ cycloalkyl, phenyl or benzyl, each phenyl and benzyl optionally substituted on the phenyl ring with halogen, C₁-C₄ alkyl, C₁-C₄ haloalkyl, C₁-C₄ alkoxy, C₁-C₄ haloalkoxy, nitro or cyano;

R¹⁸ is C₁-C₆ alkyl, C₁-C₆ haloalkyl, C₂-C₆ alkenyl, C₂-C₆ haloalkenyl, C₂-C₆ alkynyl, C₂-C₆ haloalkynyl or C₃-C₆ cycloalkyl; or R¹⁸ is phenyl or benzyl, each optionally substituted on the phenyl ring with halogen, C₁-C₄ alkyl, C₁-C₄ haloalkyl, C₁-C₄ alkoxy, C₁-C₄ haloalkoxy, nitro or cyano; and

m and n are each independently 0, 1 or 2;

provided that

i) when E is 1,2-phenylene, A is N, G is N, W is O, X is OMe, R² is CH₃ and Z substituted with R⁹ is

6-[3,5-bis(trifluoromethyl)phenyl]-4-pyrimidinyl,

6-(2,4-dichlorophenyl)-4-pyrimidinyl,

4-[3,5-bis(trifluoromethyl)phenyl]-2-pyrimidinyl,

2-[3,5-bis(trifluoromethyl)phenyl]-4-pyrimidinyl,

3-[2-(methoxycarbonyl)-6-nitrophenoxy]phenyl,

3-(2,6-dicyanophenoxy)phenyl,

3-(6-chloro-5-nitro-4-pyrimidinylloxy)phenyl,

3-[4-nitro-2-(trifluoromethyl)phenoxy]phenyl,

3-(2,6-dimethylphenoxy)phenyl,

3-(2-cyano-3-fluorophenoxy)phenyl,

3-(2-cyano-6-fluorophenoxy)phenyl, 3-(2,6-dinitrophenoxy)phenyl,

3-(2,5-difluorophenoxy)phenyl, 3-(2,5-dimethylphenoxy)phenyl,

3-(2,5-dichlorophenoxy)phenyl, 3-(3,5-dichlorophenoxy)phenyl,

3-(2,3-difluorophenoxy)phenyl, 3-(2,4-difluorophenoxy)phenyl,

3',5'-bis(trifluoromethyl)[1,1'-biphenyl]-3-yl or

3',5'-dichloro-[1,1'-biphenyl]-3-yl, then Y is other than -O-; and

ii) when E is 1,2-phenylene, A is N, G is N, W is O, X is OMe, R² is CH₃ and Z substituted with R⁹ is

3-(3,5-dichlorophenyl)-5-methyl-1,2,4-triazin-6-yl, then Y is other than -CH₂S-; and

iii) when A is N, G is N, W is O, X is OMe and EYZ is [2-[[6-[3,5-bis(trifluoromethyl)phenyl]-4-pyrimidinyl]oxy]-6-methylphenyl] or [2-[3-(2,6-difluorophenoxy)phenoxy]-6-methylphenyl], then R² is other than CH₃.

DETAILS OF THE INVENTION

In the above recitations, the term "alkyl", used either alone or in compound words such as "alkylthio" or "haloalkyl" includes straight-chain or branched alkyl, such as, methyl, ethyl, propyl, 1-methylethyl or the different butyl, pentyl or hexyl isomers.

5 "Alkenyl" includes straight-chain or branched alkenes such as vinyl, 1-propenyl, 2-propenyl, and the different butenyl, pentenyl and hexenyl isomers. "Alkenyl" also includes polyenes such as 1,2-propadienyl and 2,4-hexadienyl. "Alkynyl" includes straight-chain or branched alkynes such as ethynyl, 1-propynyl, 2-propynyl and the different butynyl, pentynyl and hexynyl isomers. "Alkynyl" can also include moieties

10 comprised of multiple triple bonds such as 2,5-hexadiynyl. "Alkylene" denotes a straight-chain alkanediyl. Examples of "alkylene" include $\text{CH}_2\text{CH}_2\text{CH}_2$, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$. "Alkenylene" denotes a straight-chain alkenediyl containing one olefinic bond. Examples of "alkenylene" include $\text{CH}_2\text{CH}=\text{CH}$, $\text{CH}_2\text{CH}_2\text{CH}=\text{CH}$, $\text{CH}_2\text{CH}=\text{CHCH}_2$ and $\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}_2$. "Alkoxy"

15 includes, for example, methoxy, ethoxy, propoxy, 1-methylethoxy and the different butoxy, pentoxy and hexyloxy isomers. "Alkoxyalkyl" denotes alkoxy substitution on alkyl. Examples of "alkoxyalkyl" include CH_3OCH_2 , $\text{CH}_3\text{OCH}_2\text{CH}_2$, $\text{CH}_3\text{CH}_2\text{OCH}_2$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{OCH}_2$ and $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_2$. "Alkoxyalkoxy" denotes alkoxy substitution on alkoxy. "Alkenyloxy" includes straight-chain or branched alkenyloxy

20 moieties. Examples of "alkenyloxy" include $\text{H}_2\text{C}=\text{CHCH}_2\text{O}$, $(\text{CH}_3)_2\text{C}=\text{CHCH}_2\text{O}$, $(\text{CH}_3)\text{CH}=\text{CHCH}_2\text{O}$, $(\text{CH}_3)\text{CH}=\text{C}(\text{CH}_3)\text{CH}_2\text{O}$ and $\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{O}$. "Alkynyloxy" includes straight-chain or branched alkynyloxy moieties. Examples of "alkynyloxy" include $\text{HC}\equiv\text{CCH}_2\text{O}$, $\text{CH}_3\text{C}\equiv\text{CCH}_2\text{O}$ and $\text{CH}_3\text{C}\equiv\text{CCH}_2\text{CH}_2\text{O}$. "Alkylthio" includes branched or straight-chain alkylthio moieties such as methylthio, ethylthio, and the

25 different propylthio, butylthio, pentylthio and hexylthio isomers. "Alkylthioalkyl" denotes alkylthio substitution on alkyl. Examples of "alkylthioalkyl" include CH_3SCH_2 , $\text{CH}_3\text{SCH}_2\text{CH}_2$, $\text{CH}_3\text{CH}_2\text{SCH}_2$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{SCH}_2$ and $\text{CH}_3\text{CH}_2\text{SCH}_2\text{CH}_2$. "Alkylthioalkylthio" denotes alkylthio substitution on alkylthio. Analogously, "alkylthioalkoxy" denotes alkylthio substitution on alkoxy.

30 "Alkylsulfinyl" includes both enantiomers of an alkylsulfinyl group. Examples of "alkylsulfinyl" include $\text{CH}_3\text{S}(\text{O})$, $\text{CH}_3\text{CH}_2\text{S}(\text{O})$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{S}(\text{O})$, $(\text{CH}_3)_2\text{CHS}(\text{O})$ and the different butylsulfinyl, pentylsulfinyl and hexylsulfinyl isomers. Examples of "alkylsulfonyl" include $\text{CH}_3\text{S}(\text{O})_2$, $\text{CH}_3\text{CH}_2\text{S}(\text{O})_2$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{S}(\text{O})_2$, $(\text{CH}_3)_2\text{CHS}(\text{O})_2$ and the different butylsulfonyl, pentylsulfonyl and hexylsulfonyl

35 isomers. "Alkenylthio" is defined analogously to the above examples. "Cycloalkyl" includes, for example, cyclopropyl, cyclobutyl, cyclopentyl, and cyclohexyl. "Trialkylsilylalkoxyalkoxy" denotes trialkylsilylalkoxy substitution on alkoxy.

Examples of "trialkylsilylalkoxyalkoxy" includes, for example, $(\text{CH}_3)_3\text{SiCH}_2\text{CH}_2\text{OCH}_2\text{O}$. "Phenylene" denotes $-(\text{C}_6\text{H}_4)-$.

One skilled in the art will appreciate that not all nitrogen containing heterocycles can form *N*-oxides since the nitrogen requires an available lone pair for oxidation to the oxide; one skilled in the art will recognize those nitrogen containing heterocycles which can form *N*-oxides.

The term "halogen", either alone or in compound words such as "haloalkyl", includes fluorine, chlorine, bromine or iodine. The term "1-2 halogen" indicates that one or two of the available positions for that substituent may be halogen which are independently selected. Further, when used in compound words such as "haloalkyl", said alkyl may be partially or fully substituted with halogen atoms which may be the same or different. Examples of "haloalkyl" include F_3C , ClCH_2 , CF_3CH_2 and CF_3CCl_2 . The terms "haloalkenyl", "haloalkynyl", "haloalkoxy", and the like, are defined analogously to the term "haloalkyl". Examples of "haloalkenyl" include $(\text{Cl})_2\text{C}=\text{CHCH}_2$ and $\text{CF}_3\text{CH}_2\text{CH}=\text{CHCH}_2$. Examples of "haloalkynyl" include $\text{HC}\equiv\text{CCHCl}$, $\text{CF}_3\text{C}\equiv\text{C}$, $\text{CCl}_3\text{C}\equiv\text{C}$ and $\text{FCH}_2\text{C}\equiv\text{CCH}_2$. Examples of "haloalkoxy" include CF_3O , $\text{CCl}_3\text{CH}_2\text{O}$, $\text{HCF}_2\text{CH}_2\text{CH}_2\text{O}$ and $\text{CF}_3\text{CH}_2\text{O}$. Examples of "haloalkylthio" include CCl_3S , CF_3S , $\text{CCl}_3\text{CH}_2\text{S}$ and $\text{ClCH}_2\text{CH}_2\text{CH}_2\text{S}$. Examples of "haloalkylsulfinyl" include $\text{CF}_3\text{S}(\text{O})$, $\text{CCl}_3\text{S}(\text{O})$, $\text{CF}_3\text{CH}_2\text{S}(\text{O})$ and $\text{CF}_3\text{CF}_2\text{S}(\text{O})$. Examples of "haloalkylsulfonyl" include $\text{CF}_3\text{S}(\text{O})_2$, $\text{CCl}_3\text{S}(\text{O})_2$, $\text{CF}_3\text{CH}_2\text{S}(\text{O})_2$ and $\text{CF}_3\text{CF}_2\text{S}(\text{O})_2$.

The total number of carbon atoms in a substituent group is indicated by the " $\text{C}_i\text{-C}_j$ " prefix where *i* and *j* are numbers from 1 to 10. For example, $\text{C}_1\text{-C}_3$ alkylsulfonyl designates methylsulfonyl through propylsulfonyl. Examples of "alkylcarbonyl" include $\text{CH}_3\text{C}(=\text{O})$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}(=\text{O})$ and $(\text{CH}_3)_2\text{CHC}(=\text{O})$. Examples of "alkoxycarbonyl" include $\text{CH}_3\text{OC}(=\text{O})$, $\text{CH}_3\text{CH}_2\text{OC}(=\text{O})$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{OC}(=\text{O})$, $(\text{CH}_3)_2\text{CHOC}(=\text{O})$ and the different butoxy- or pentoxycarbonyl isomers. In the above recitations, when a compound of Formula I is comprised of one or more aromatic or heterocyclic rings, all substituents are attached to these rings through any available carbon by replacement of a hydrogen on said carbon.

When a group contains a substituent which can be hydrogen, for example R^5 or R^6 , then, when this substituent is taken as hydrogen, it is recognized that this is equivalent to said group being unsubstituted.

Compounds of this invention can exist as one or more stereoisomers. The various stereoisomers include enantiomers, diastereomers, atropisomers and geometric isomers. One skilled in the art will appreciate that one stereoisomer may be more active and/or may exhibit beneficial effects when enriched relative to the other stereoisomer(s) or when separated from the other stereoisomer(s). (See, e.g., U.S. Provisional Patent

Application Serial No. _____ [Docket No. BA-9183-P1] filed September 4, 1997, which is hereby incorporated by reference in its entirety.) Additionally, the skilled artisan knows how to separate, enrich, and/or to selectively prepare said stereoisomers. Accordingly, the present invention comprises compounds selected from Formula I,
5 *N*-oxides and agriculturally suitable salts thereof. The compounds of the invention may be present as a mixture of stereoisomers, individual stereoisomers or as an optically active form.

The salts of the compounds of the invention include acid-addition salts with inorganic or organic acids such as hydrobromic, hydrochloric, nitric, phosphoric,
10 sulfuric, acetic, butyric, fumaric, lactic, maleic, malonic, oxalic, propionic, salicylic, tartaric, 4-toluenesulfonic or valeric acids. The salts of the compounds of the invention also include those formed with organic bases (e.g., pyridine, ammonia or triethylamine) or inorganic bases (e.g., hydrides, hydroxides or carbonates of sodium, potassium, lithium, calcium, magnesium or barium) when the compound contains an acidic group
15 such as a phenol.

Preferred compounds for reasons of better activity and/or ease of synthesis are:

Preferred 1. Compounds of Formula I above, and agriculturally suitable salts thereof, wherein:

- 20 A is O, S or NR⁵;
G is C;
R⁹ is phenyl, phenylmethyl, benzoyl, phenoxy, pyridinyl, pyridinyloxy, thienyl, thienyloxy, furanyl, pyrimidinyl or pyrimidinyloxy, each substituted on the aromatic ring with two or more R¹¹ and with one R¹²; and
25 R¹² is halogen, C₁-C₄ alkyl, C₁-C₄ haloalkyl, C₁-C₄ alkoxy, C₁-C₄ haloalkoxy, C₁-C₄ alkylthio, C₁-C₄ haloalkylthio, C₁-C₄ alkylsulfinyl, C₁-C₄ haloalkylsulfinyl, C₁-C₄ alkylsulfonyl, C₁-C₄ haloalkylsulfonyl, nitro, cyano, thiocyanato, hydroxy or N(R¹⁷)₂; or
30 R¹² is phenyl optionally substituted with halogen, C₁-C₄ alkyl, C₁-C₄ haloalkyl, C₁-C₄ alkoxy, C₁-C₄ haloalkoxy, nitro or cyano.

Preferred 2. Compounds of Preferred 1 wherein:

- 35 A is O;
W is O;
X is OR¹;
R¹ is CH₃;
R² is CH₃;
R³ and R⁴ are each independently halogen or C₁-C₃ alkyl; and
Y is O, CH₂O or CH₂S(O)_n.

Preferred 3. Compounds of Formula I above, and agriculturally suitable salts thereof, wherein:

A is N or CR⁶;

G is N;

5 R⁹ is phenyl, phenylmethyl, benzoyl, phenoxy, pyridinyl, pyridinyloxy, thienyl, thienyloxy, furanyl, pyrimidinyl; or pyrimidinyloxy each substituted on the aromatic ring with two or more R¹¹ and with one R¹²; and

10 R¹² is halogen, C₁-C₄ alkyl, C₁-C₄ haloalkyl, C₁-C₄ alkoxy, C₁-C₄ haloalkoxy, C₁-C₄ alkylthio, C₁-C₄ haloalkylthio, C₁-C₄ alkylsulfinyl, C₁-C₄ haloalkylsulfinyl, C₁-C₄ alkylsulfonyl, C₁-C₄ haloalkylsulfonyl, nitro, cyano, thiocyanato, hydroxy or N(R¹⁷)₂; or R¹² is phenyl optionally substituted with halogen, C₁-C₄ alkyl, C₁-C₄ haloalkyl, C₁-C₄ alkoxy, C₁-C₄ haloalkoxy, nitro or cyano.

15 Preferred 4. Compounds of Preferred 3 wherein:

A is N;

W is O;

X is OR¹;

R¹ is CH₃;

20 R² is CH₃;

R³ and R⁴ are each independently halogen or C₁-C₃ alkyl; and

Y is O, CH₂O or CH₂S(O)_n.

Of note are compounds where R¹¹ and R¹² are halogen. Where there is one R¹¹ group, the 2,3-dihalo, 2,4-dihalo, 2,5-dihalo, 2,6-dihalo, 3,4-dihalo and 3,5-dihalo
25 compounds (e.g. 2,3-difluoro, 2,4-difluoro, 2,5-difluoro, 2,6-difluoro, 2-chloro-6-fluoro and 2,6-dichloro) are of particular note. Where there are two R¹¹ groups, the 2,3,4-trihalo, 2,3,5-trihalo, 2,3,6-trihalo, 2,4,5-trihalo, 2,4,6-trihalo and 3,4,5-trihalo
compounds (e.g. 2,4,6-trifluoro, 2,3,4-trifluoro, 2,3,5-trifluoro, 2,3,6-trifluoro, 2,3,6-trifluoro, 2,6-dichloro-4-fluoro and 2,4,6-trichloro) are of particular note. Where there
30 are three R¹¹ groups, the 2,3,4,5-tetrahalo and 2,3,5,6-tetrahalo compounds (e.g. 2,3,5,6-tetrafluoro and 2,3,5,6-tetrachloro) are of particular note.

Also of note are compounds where there are at least two R¹¹ groups. This includes compounds where at least two of the total R¹¹ and R¹² groups are other than halogen (e.g. 2,6-diR¹¹-4-R¹² and 2,4-diR¹¹-6-R¹² compounds where each R¹¹ is other
35 than halogen or where one R¹¹ and R¹² are other than halogen). Compounds where there are at least two R¹¹ groups also include compounds having two halogen substituents (e.g. 2,6-dihalo-4-R¹² and 2,4-dihalo-6-R¹²) where R¹² is other than halogen.

Of particular note when there are a total of two R^{11} and R^{12} groups are 2,6-; 2,5-; 2,4-; and 2,3- positioning. Of particular note when there are a total of three R^{11} and R^{12} groups are 2,3,4-; 2,3,5-; 2,3,6-; 2,4,5-; and 2,4,6- positioning. Of particular note when there are a total of four R^{11} and R^{12} groups is 2,3,5,6 positioning.

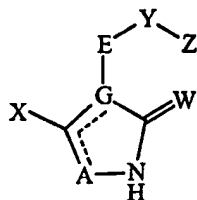
- 5 This invention also relates to fungicidal compositions comprising fungicidally effective amounts of the compounds of the invention and at least one of a surfactant, a solid diluent or a liquid diluent. The preferred compositions of the present invention are those which comprise the above preferred compounds.

- 10 This invention also relates to a method for controlling plant diseases caused by fungal plant pathogens comprising applying to the plant or portion thereof, or to the plant seed or seedling, a fungicidally effective amount of the compounds of the invention (e.g., as a composition described herein). The preferred methods of use are those involving the above preferred compounds.

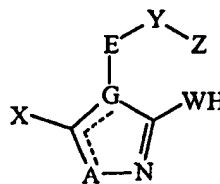
SYNTHESIS DETAILS

- 15 The compounds of Formula I can be prepared by one or more of the following methods and variations as described in Schemes 1-22. One skilled in the art will recognize that compounds of Formula Ia and Ib are encompassed by Formula I and, therefore, can be prepared by these procedures. The definitions of E, A, G, W, X, R, R^1 - R^{20} , Y, Z, m and n in the compounds of Formulae 1-36 below are as defined above
 20 (including the Summary of the Invention) or below. Compounds of Formulae Ia-Ih are various subsets of the compounds of Formula I, and all substituents for Formulae Ia-Ih are as defined above for Formula I.

- One skilled in the art will recognize that some compounds of Formula I can exist in one or more tautomeric forms. For example, a compound of Formula I wherein R^2 is
 25 H may exist as tautomer Ia or Ib, or both Ia and Ib. The present invention comprises all tautomeric forms of compounds of Formula I.



Ia

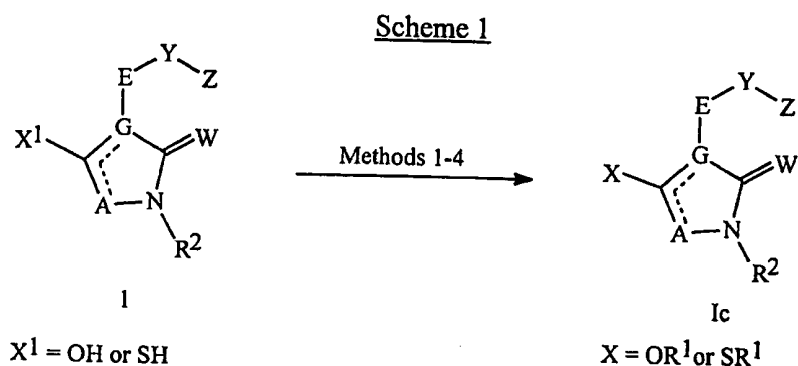


Ib

- The compounds of Formula I can be prepared as described below in Procedures 1) to 5). Procedures 1) to 4) describe syntheses involving construction of the amide ring after the formation of the aryl moiety (E-Y-Z). Procedure 5) describes syntheses of the
 30 aryl moiety (E-Y-Z) with the amide ring already in place.

1) Alkylation Procedures

The compounds of Formula Ic are prepared by treating compounds of Formula 1 with an appropriate alkyl transfer reagent in an inert solvent with or without additional acidic or basic reagents or other reagents (Scheme 1). Suitable solvents are selected from the group consisting of polar aprotic solvents such as acetonitrile, dimethylformamide or dimethyl sulfoxide; ethers such as tetrahydrofuran, dimethoxyethane, or diethyl ether; ketones such as acetone or 2-butanone; hydrocarbons such as toluene or benzene; and halocarbons such as dichloromethane or chloroform.



Method 1: U-CH=N_2 (U = H or $(\text{CH}_3)_3\text{Si}$)
2

Method 2: $\text{Cl}_3\text{C-C(=NH)-OR}^1$; Lewis acid
3

Method 3: $(\text{R}^1)_3\text{O}^+ \text{BF}_4^-$
4

Method 4: $(\text{R}^1)_2\text{SO}_4$; $\text{R}^1\text{OSO}_2\text{V}$; or $\text{R}^1\text{-hal}$;
optional base
(hal = F, Cl, Br, or I)
(V = $\text{C}_1\text{-C}_6$ alkyl, $\text{C}_1\text{-C}_6$ haloalkyl, or 4- $\text{CH}_3\text{-C}_6\text{H}_4$)

For example, compounds of Formula Ic can be prepared by the action of diazoalkane reagents of Formula 2 such as diazomethane (U = H) or trimethylsilyldiazomethane (U = $(\text{CH}_3)_3\text{Si}$) on compounds of Formula 1 (Method 1). Use of trimethylsilyldiazomethane requires a protic cosolvent such as methanol. For examples of these procedures, see *Chem. Pharm. Bull.*, (1984), 32, 3759.

As indicated in Method 2, compounds of Formula Ic can also be prepared by contacting compounds of Formula 1 with alkyl trichloroacetimidates of Formula 3 and a Lewis acid catalyst. Suitable Lewis acids include trimethylsilyl triflate and tetrafluoroboric acid. The alkyl trichloroacetimidates can be prepared from the

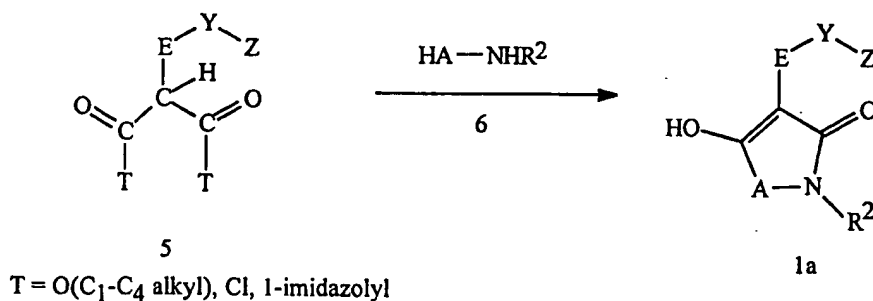
appropriate alcohol and trichloroacetonitrile as described in the literature (J. Danklmaier and H. Hömig, *Synth. Commun.*, (1990), 20, 203).

Compounds of Formula 1c can also be prepared from compounds of Formula 1 by treatment with a trialkyloxonium tetrafluoroborate (i.e., Meerwein's salt) of Formula 4 (Method 3). The use of trialkyloxonium salts as powerful alkylating agents is well known in the art (see U. Schöllkopf, U. Groth, C. Deng, *Angew. Chem., Int. Ed. Engl.*, (1981), 20, 798).

Other alkylating agents which can convert carbonyl compounds of Formula 1 to compounds of Formula 1c are dialkyl sulfates such as dimethyl sulfate, haloalkyl sulfonates such as methyl trifluoromethanesulfonate, and alkyl halides such as iodomethane and propargyl bromide (Method 4). These alkylations can be conducted with or without additional base. Appropriate bases include alkali metal alkoxides such as potassium *tert*-butoxide, inorganic bases such as sodium hydride and potassium carbonate, or tertiary amines such as triethylamine, pyridine, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), and triethylenediamine. See R. E. Benson, T. L. Cairns, *J. Am. Chem. Soc.*, (1948), 70, 2115 for alkylation examples using agents of this type.

Compounds of Formula 1a (compounds of Formula 1 wherein G = C, W = O and X¹ = OH) can be prepared by condensation of malonates or malonate derivatives of Formula 5 with an ambident nucleophile of Formula 6 (Scheme 2). The nucleophiles of Formula 6 are *N*-substituted hydroxylamines (HO-NHR²) and substituted hydrazines (HN(R⁵)-NHR²). Examples of such nucleophiles are *N*-methylhydroxylamine and methylhydrazine. The malonate esters of Formula 5 can be prepared by methods described hereinafter. The esters of Formula 5 can also be activated by first hydrolyzing the ester to form the corresponding carboxylic acid, and then converting the acid into the acid chloride (T = Cl) using thionyl chloride or oxalyl chloride, or into the acyl imidazole (T = 1-imidazolyl) by treating with 1,1'-carbonyldiimidazole.

Scheme 2

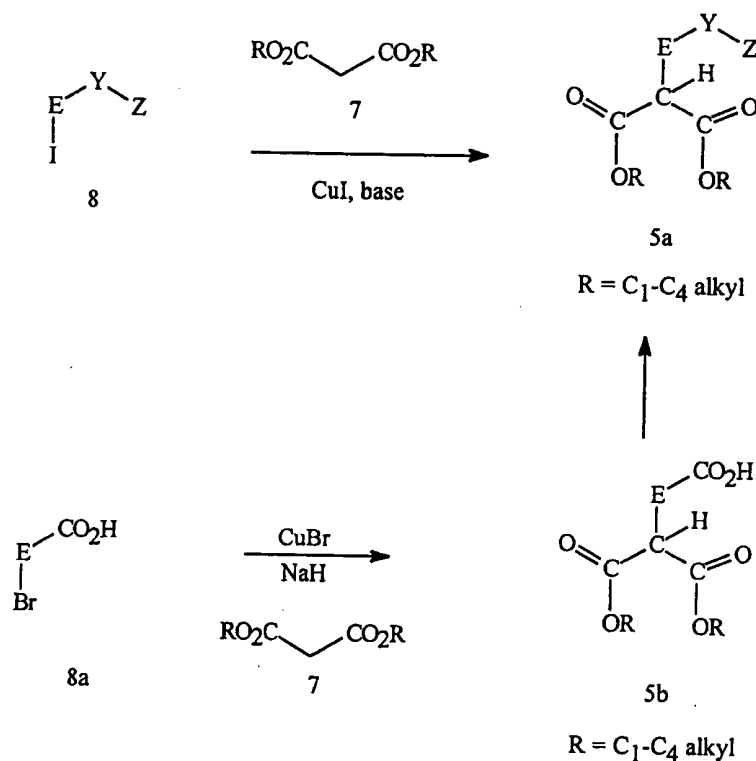


Esters of Formula 5a can be prepared from copper (I)-catalyzed reaction of malonate esters of Formula 7 with substituted aryl halides of Formula 8 according to

methods adapted from A. Osuka, T. Kobayashi and H. Suzuki, *Synthesis*, (1983), 67 and M. S. Malamas, T. C. Hohman, and J. Millen, *J. Med. Chem.*, 1994, 37, 2043-2058, and illustrated in Scheme 3.

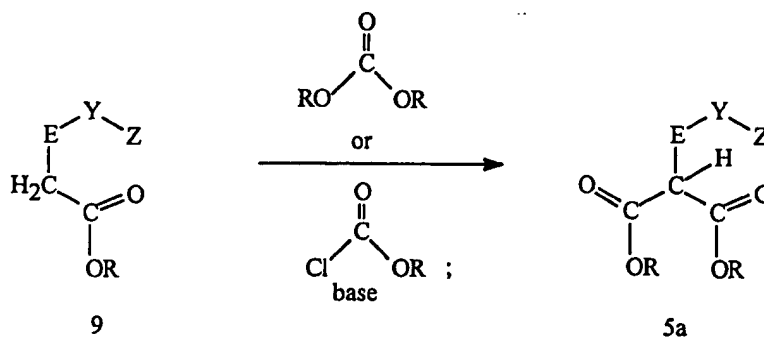
Malonate esters of Formula 5a can also be prepared from diester carboxylic acids of Formula 5b after modification of the carboxylic acid functional group to the appropriate Y and Z group. A copper (I)-catalyzed coupling of malonates of Formula 7 with orthobromocarboxylic acids of Formula 8a (see A. Bruggink, A. McKillop, *Tetrahedron*, (1975), 31, 2607) can be used to prepare compounds of Formula 5b as shown in Scheme 3. Methods to prepare compounds of Formula 8a are common in the art (see P. Beak, V. Snieckus, *Acc. Chem. Res.*, (1982), 15, 306 and *Org. React.*, (1979), 26, 1 and references therein).

Scheme 3



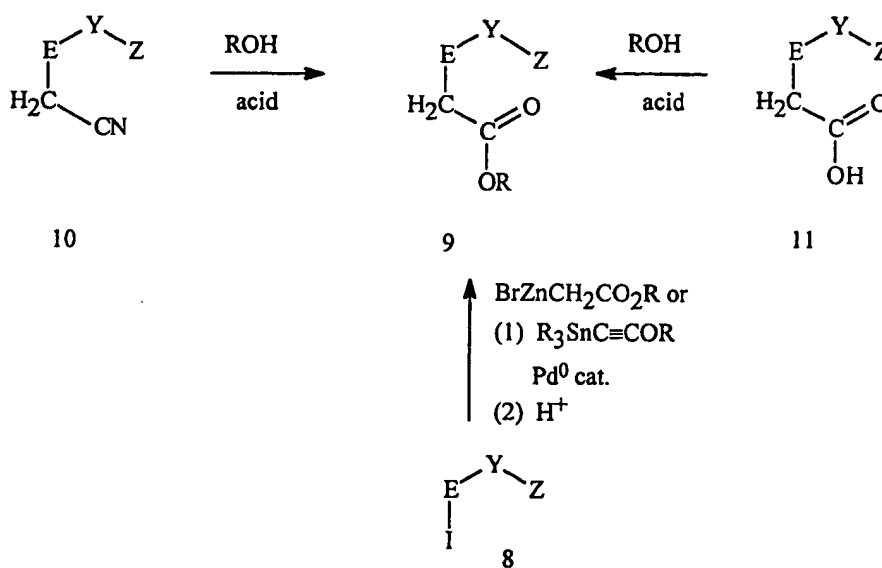
Additionally, the malonate esters of Formula 5a can be prepared by treating aryl acetic acid esters of Formula 9 with a dialkyl carbonate or alkyl chloroformate in the presence of a suitable base such as, but not limited to, sodium metal or sodium hydride (Scheme 4). For example, see *J. Am. Chem. Soc.*, (1928), 50, 2758.

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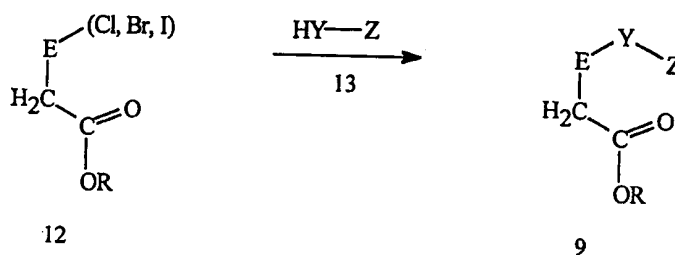
Scheme 4R = C₁-C₄ alkyl

Esters of Formula 9 can be prepared from acid-catalyzed alcoholysis of aryl acetonitriles of Formula 10 or esterification of aryl acetic acids of Formula 11 as illustrated in Scheme 5 (see *Org. Synth.*, Coll. Vol. I, (1941), 270).

5 Additionally, esters of formula 9 can be prepared by palladium (0)-catalyzed cross coupling reaction of aryl iodides of Formula 8 with a Reformatsky reagent or an alkoxy(trialkylstannyl)acetylene followed by hydration (Scheme 5). For example, see T. Sakamoto, A. Yasuhara, Y. Kondo, H. Yamanaka, *Synlett*, (1992), 502, and J. F. Fauvarque, A. Jutard, *J. Organometal. Chem.*, (1977), 132, C17.

Scheme 5R = C₁-C₄ alkyl

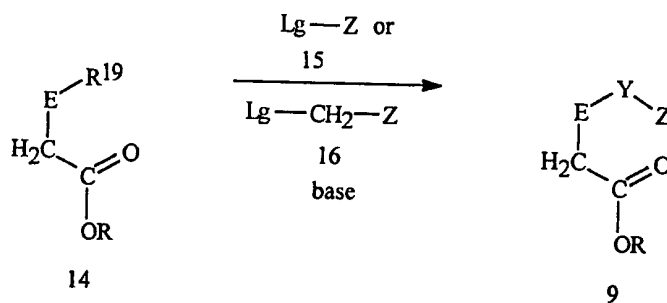
Aryl acetic acid esters of Formula 9 can also be prepared by copper (I)-catalyzed condensation of aryl halides of Formula 12 with compounds of Formula 13 as described in EP-A-307,103 and illustrated below in Scheme 6.

Scheme 6

$\text{R} = \text{C}_1\text{-C}_4$ alkyl

$\text{Y} = \text{O, S, NR}^7$

- 5 Some esters of Formula 9 can also be prepared by forming the Y bridge using conventional nucleophilic substitution chemistry (Scheme 7). Displacement of an appropriate leaving group (Lg) in electrophiles of Formula 15 or 16 with a nucleophilic ester of Formula 14 affords compounds of Formula 9. A base, for example sodium hydride, is used to generate the corresponding alkoxide or thioalkoxide of the compound of Formula 14.

Scheme 7

$\text{R} = \text{C}_1\text{-C}_4$ alkyl

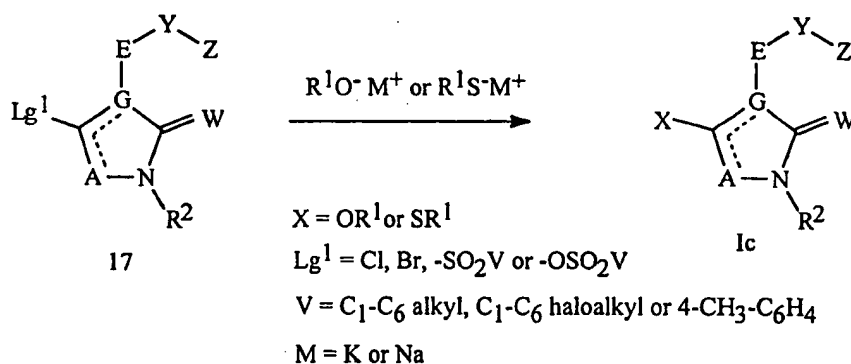
$\text{R}^{19} = \text{OH, SH, CH}_2\text{OH, CH}_2\text{SH, NHR}^7$

$\text{Y} = \text{O, S, CH}_2\text{O, CH}_2\text{S, NR}^7$

$\text{Lg} = \text{Br, Cl, I, OSO}_2\text{CH}_3, \text{OSO}_2(4\text{-Me-Ph})$

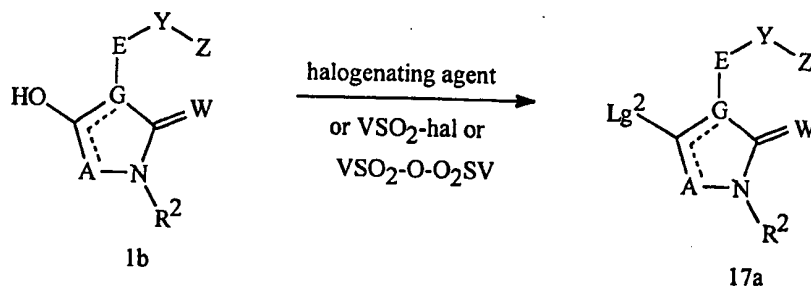
2) Displacement and Conjugate Addition/Elimination Procedures

- Compounds of Formula Ic can also be prepared by reaction of Formula 17 compounds with alkali metal alkoxides ($R^1O^-M^+$) or an alkali metal thioalkoxides ($R^1S^-M^+$), (Scheme 8). The leaving group Lg^1 in the amides of Formula 17 are any group known in the art to undergo a displacement reaction of this type. Examples of suitable leaving groups include chlorine, bromine, and sulfonyl and sulfonate groups. Examples of suitable inert solvents are dimethylformamide or dimethyl sulfoxide, dimethoxyethane methanol.

Scheme 8

- Compounds of Formula 17a can be prepared from compounds of Formula 1b (compounds of Formula 1 wherein X^1 is OH) by reaction with halogenating agents such as thionyl chloride or phosphorus oxybromide to form the corresponding β -halo-substituted derivatives (Scheme 9). Compounds of Formula 17a when Lg^2 is chlorine or bromine are also compounds of Formula Id (compounds of Formula I where X is halogen). Alternatively, compounds of Formula 1b can be treated with an alkylsulfonyl halide or haloalkylsulfonyl anhydride, such as methanesulfonyl chloride, *p*-toluenesulfonyl chloride, and trifluoromethanesulfonyl anhydride, to form the corresponding β -alkylsulfonate of Formula 17a. The reaction with the sulfonyl halides may be performed in the presence of a suitable base (e.g., triethylamine).

16

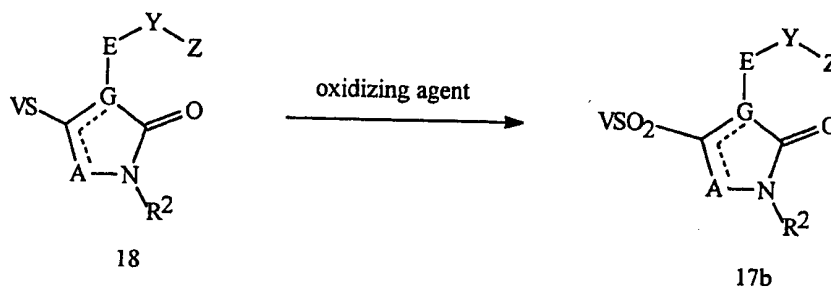
Scheme 9

$\text{Lg}^2 = \text{Cl, Br or } -\text{OSO}_2\text{V}$

$\text{V} = \text{C}_1\text{-C}_6 \text{ alkyl, C}_1\text{-C}_6 \text{ haloalkyl or 4-CH}_3\text{-C}_6\text{H}_4$

$\text{hal} = \text{Br, Cl or F}$

As illustrated in Scheme 10, sulfonyl compounds of Formula 17b can be prepared by oxidation of the corresponding thio compound of Formula 18 using well-known methods for the oxidation of sulfur (see Schrenk, K. In *The Chemistry of Sulphones and Sulphoxides*; Patai, S. et al., Eds.; Wiley: New York, 1988). Suitable oxidizing reagents include meta-chloroperoxybenzoic acid, hydrogen peroxide and Oxone® (KHSO₅).

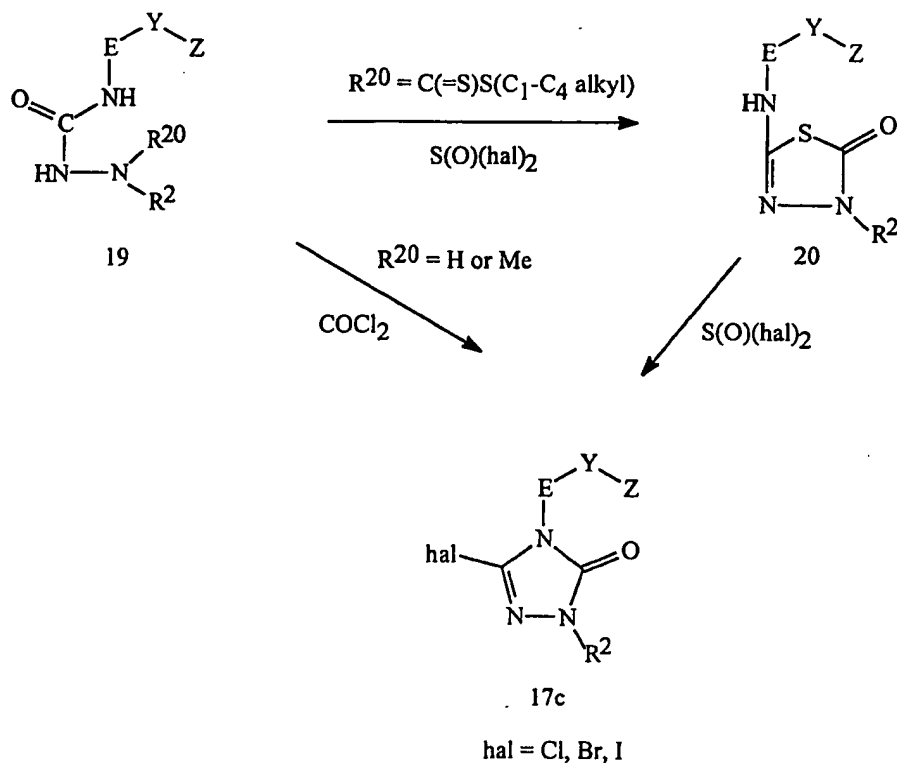
Scheme 10

$\text{V} = \text{C}_1\text{-C}_6 \text{ alkyl, C}_1\text{-C}_6 \text{ haloalkyl or 4-CH}_3\text{-C}_6\text{H}_4$

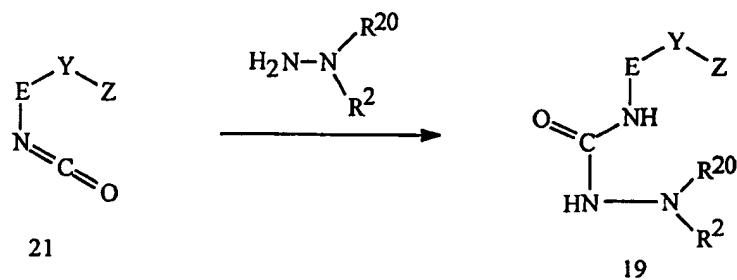
Alternatively, halo-compounds of Formula 17c (compounds of Formula 17a wherein $\text{A} = \text{N}$, $\text{G} = \text{N}$, and $\text{W} = \text{O}$) can be prepared from hydrazides of Formula 19 as illustrated in Scheme 11. When $\text{R}^{20} = \text{C}(=\text{S})\text{S}(\text{C}_1\text{-C}_4 \text{ alkyl})$, the compound of Formula 19 is treated with, for example, excess thionyl chloride, the product formed first is the ring-closed compound of Formula 20. This compound can be isolated or converted *in situ* to the compound of Formula 17c; see P. Molina, A. Tárraga, A. Espinosa, *Synthesis*, (1989), 923 for a description of this process.

Alternatively, when $\text{R}^{20} = \text{H}$ or Me the hydrazide of Formula 19 is cyclized with phosgene to form the cyclic urea of Formula 17c wherein $\text{hal} = \text{Cl}$. This procedure is described in detail in *J. Org. Chem.*, (1989), 54, 1048.

17

Scheme 11

The hydrazides of Formula 19 can be prepared as illustrated in Scheme 12. Condensation of the isocyanate of Formula 21 with the hydrazine of Formula $\text{H}_2\text{NNR}^{20}\text{R}^2$ in an inert solvent such as tetrahydrofuran affords the hydrazide.

Scheme 12

$\text{R}^{20} = \text{C}(=\text{S})\text{S}(\text{C}_1\text{-C}_4 \text{ alkyl}), \text{H or Me}$

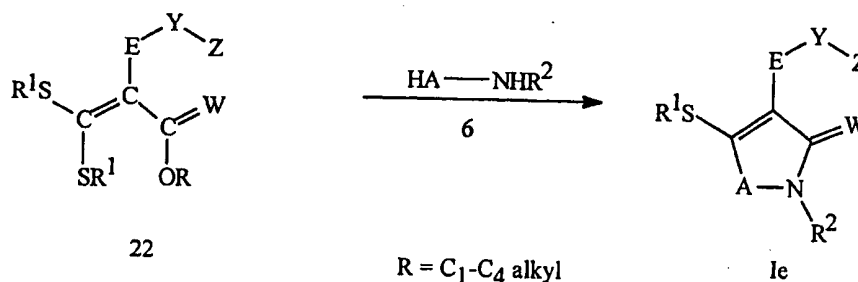
3) Conjugate Addition/Cyclization Procedures

5

In addition to the methods disclosed above, compounds of Formula I wherein $\text{X} = \text{SR}^1$ and $\text{G} = \text{C}$ (Formula 1e) can be prepared by treating a ketenedithioacetal of Formula 22 with an ambident nucleophile of Formula 6 (Scheme 13). The nucleophiles of Formula 6 are described above.

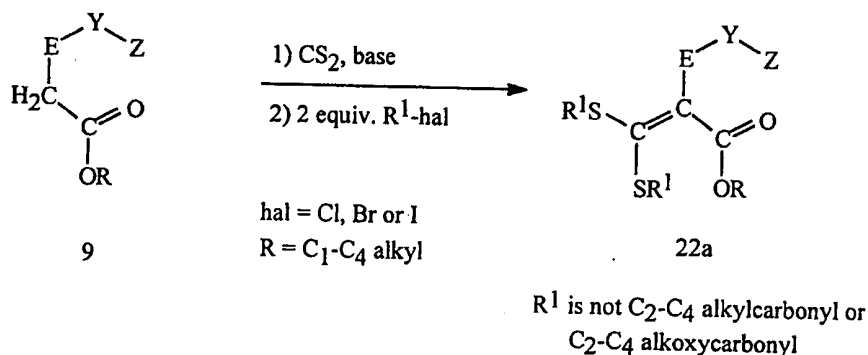
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Scheme 13



Ketene dithioacetals of Formula 22a can be prepared by condensing arylacetic acid esters of Formula 9 with carbon disulfide in the presence of a suitable base, followed by reaction with two equivalents of an R¹-halide, such as iodomethane or propargyl bromide (Scheme 14).

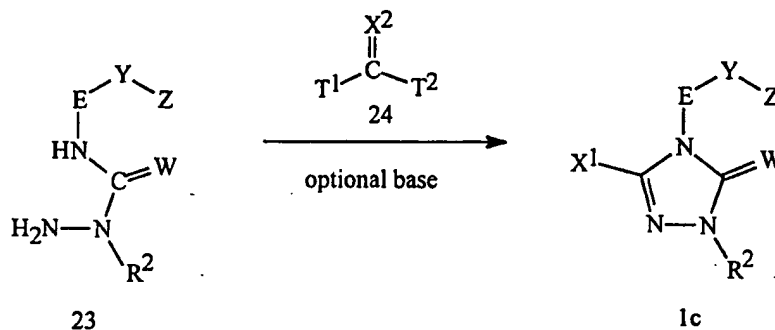
Scheme 14



- 5 Compounds of Formula 1c (compounds of Formula 1 wherein A = N, G = N) can be prepared by condensation of *N*-amino-ureas of Formula 23 with a carbonylating agent of Formula 24 (Scheme 15). The carbonylating agents of Formula 24 are carbonyl or thiocarbonyl transfer reagents such as phosgene, thiophosgene, diphosgene (ClC(=O)OCCl₃), triphosgene (Cl₃COC(=O)OCCl₃), *N,N'*-carbonyldiimidazole, *N,N'*-thiocarbonyldiimidazole, and 1,1'-carbonyldi(1,2,4-triazole). Alternatively, the compounds of Formula 24 can be alkyl chloroformates or dialkyl carbonates. Some of these carbonylating reactions may require the addition of a base to effect reaction. Appropriate bases include alkali metal alkoxides such as potassium *tert*-butoxide, inorganic bases such as sodium hydride and potassium carbonate, tertiary amines such as triethylamine and triethylenediamine, pyridine, or 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). Suitable solvents include polar aprotic solvents such as acetonitrile, dimethylformamide, or dimethyl sulfoxide; ethers such as tetrahydrofuran, dimethoxyethane, or diethyl ether; ketones such as acetone or 2-butanone; hydrocarbons such as toluene or benzene; or halocarbons such as dichloromethane or chloroform. The
- 10
- 15

reaction temperature can vary between 0°C and 150°C and the reaction time can be from 1 to 72 hours depending on the choice of base, solvent, temperature, and substrates.

Scheme 15



T¹ and T² are independently Cl, OCCl₃, O(C₁-C₄ alkyl), 1-imidazolyl, 1,2,4-triazolyl

X¹ = OH or SH

X² = O or S

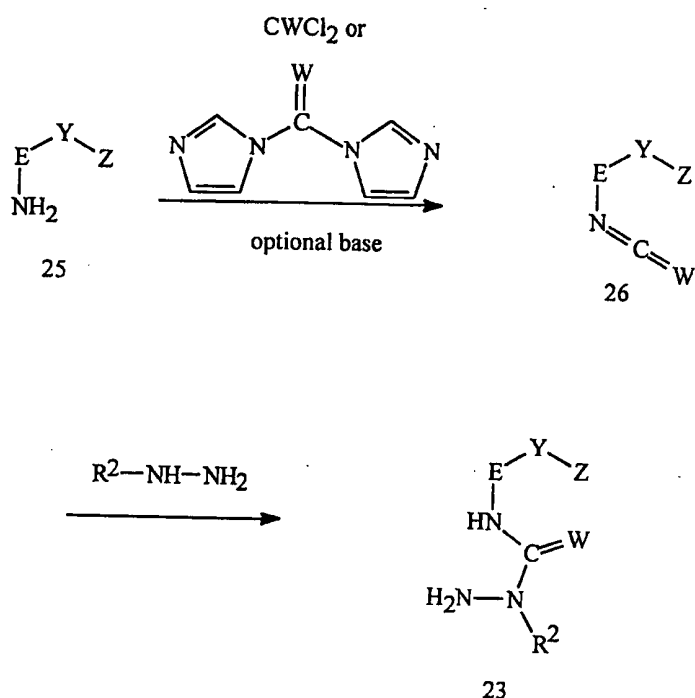
N-Amino-ureas of Formula 23 can be prepared as illustrated in Scheme 16.

Treatment of an arylamine of Formula 25 with phosgene, thiophosgene,

- 5 *N,N'*-carbonyldiimidazole, or *N,N'*-thiocarbonyldiimidazole produces the isocyanate or isothiocyanate of Formula 26. A base can be added for reactions with phosgene or thiophosgene. Subsequent treatment of the iso(thio)cyanate with an R²-substituted hydrazine produces the *N*-amino-urea of Formula 23.

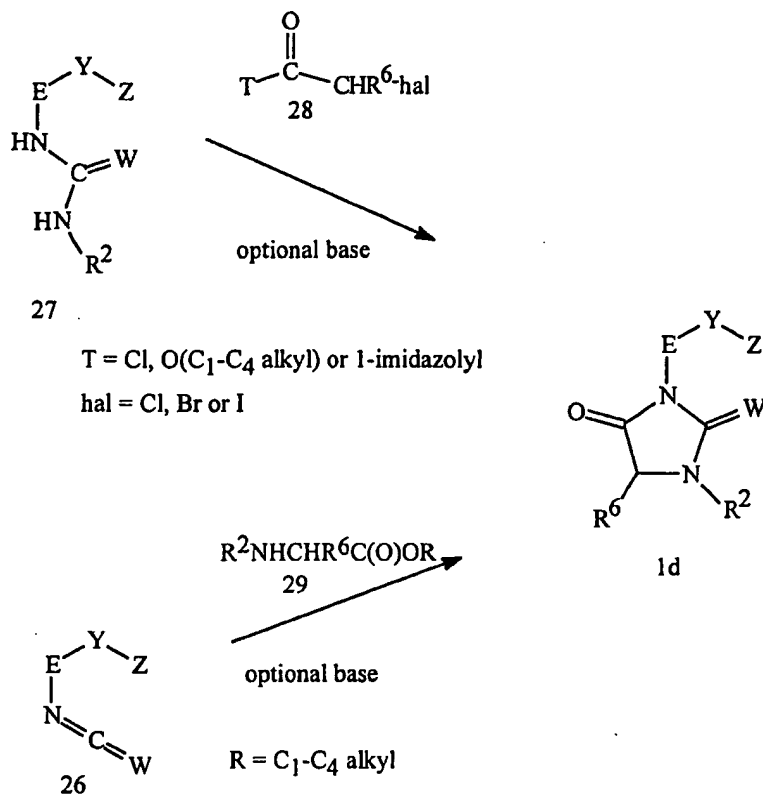
20

Scheme 16



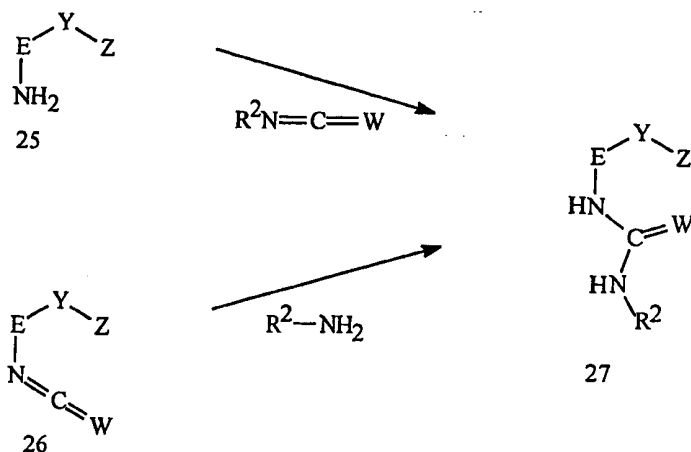
- Compounds of Formula 1d (compounds of Formula 1 wherein A = CR⁶, G = N, and X¹ = O) can be prepared by either method illustrated in Scheme 17. Ureas of Formula 27 are reacted with activated 2-halocarboxylic acid derivatives 28 such as 2-halocarboxylic acid chlorides, 2-halocarboxylic acid esters or 2-haloacyl imidazoles.
- 5 The initial acylation on the arylamino nitrogen is followed by an intramolecular displacement of the 2-halo group to effect cyclization. Base may be added to accelerate the acylation and/or the subsequent cyclization. Suitable bases include triethylamine and sodium hydride. Alternatively, Formula 1d compounds can be prepared by reaction of Formula 26 isocyanates with Formula 29 esters. As described above, base may be
- 10 added to accelerate the reaction and subsequent cyclization to Formula 1d compounds.

21

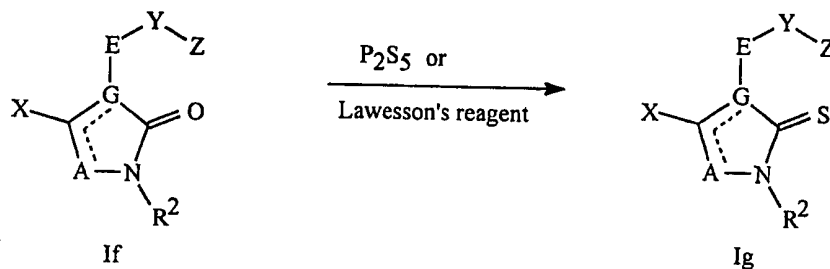
Scheme 17

The ureas of Formula 27 can be prepared by either of the methods illustrated in Scheme 18. The arylamine of Formula 25 can be contacted with an isocyanate or isothiocyanate of Formula $\text{R}^2\text{N}=\text{C}=\text{W}$ as described above. Alternatively, an isocyanate or isothiocyanate of Formula 26 can be condensed with an amine of Formula $\text{R}^2\text{-NH}_2$ to form the urea. The arylamine and iso(thio)cyanates of Formulae 25 and 26, respectively, are commercially available or prepared by well-known methods. For example, isothiocyanates can be prepared by methods described in *J. Heterocycl. Chem.*, (1990), 27, 407. Isocyanates can be prepared as described in March, J. *Advanced Organic Chemistry*; 3rd ed., John Wiley: New York, (1985), pp 944, 1166 and also in *Synthetic Communications*, (1993), 23(3), 335 and references therein. For methods describing the preparation of arylamines of Formula 25 that are not commercially available, see M. S. Gibson In *The Chemistry of the Amino Group*; Patai, S., Ed.; Interscience Publishers, 1968; p 37 and *Tetrahedron Lett.* (1982), 23(7), 699 and references therein.

22

Scheme 184) Thionation Procedures

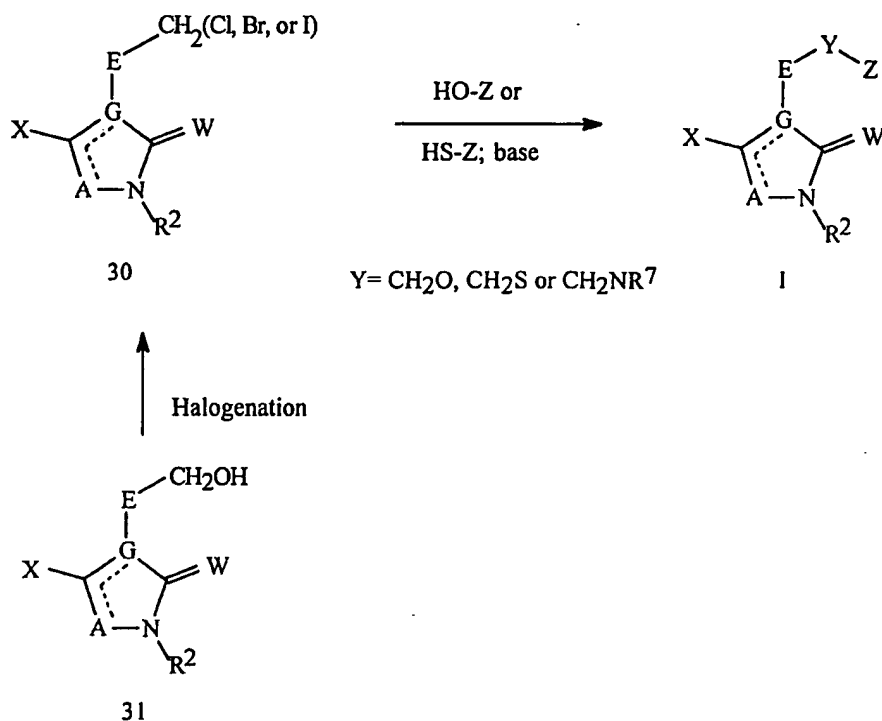
Compounds of Formula Ig, compounds of Formula I wherein W = S, can be prepared by treating compounds of Formula If (I wherein W = O) with thionating reagents such as P₂S₅ or Lawesson's reagent (2,4-bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane-2,4-disulfide) as illustrated in Scheme 19 (see *Bull. Soc. Chim. Belg.*, (1978), 87, 229; and *Tetrahedron Lett.*, (1983), 24, 3815).

Scheme 195) Aryl Moiety (E-Y-Z) Synthesis Procedures

Compounds of Formula I (wherein Y is CH₂O, CH₂S, or CH₂NR⁷) can be prepared by contacting halides of Formula 30 with various nucleophiles (Scheme 20).

- 10 The appropriate alcohol or thiol is treated with a base, for example sodium hydride, to form the corresponding alkoxide or thioalkoxide which acts as the nucleophile. The halides of Formula 30 can be prepared from the alcohols of Formula 31 with halogenating reagents such as thionyl chloride.

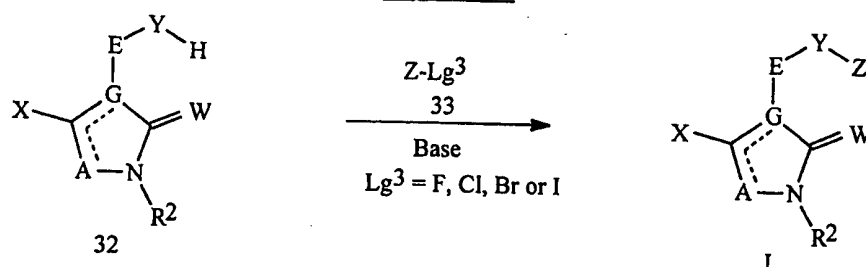
23

Scheme 20

The compounds of the present invention are prepared by combinations of reactions as illustrated in the Schemes 1-20 in which Z is a moiety as described in the summary. Preparation of the compounds containing the radical Z as described in the summary, substituted with R^9 (defined as any group attached to Z as depicted in each of the individual schemes) can be accomplished by one skilled in the art by the appropriate combination of reagents and reaction sequences for a particular Z- R^9 . Such reaction sequences can be developed based on known reactions available in the chemical art. For a general reference, see March, *J. Advanced Organic Chemistry*, 3rd ed., John Wiley: New York, (1985) and references therein. See the following paragraphs for some examples of how R^9 is defined in individual schemes, and the preparation of representative Z- R^9 examples.

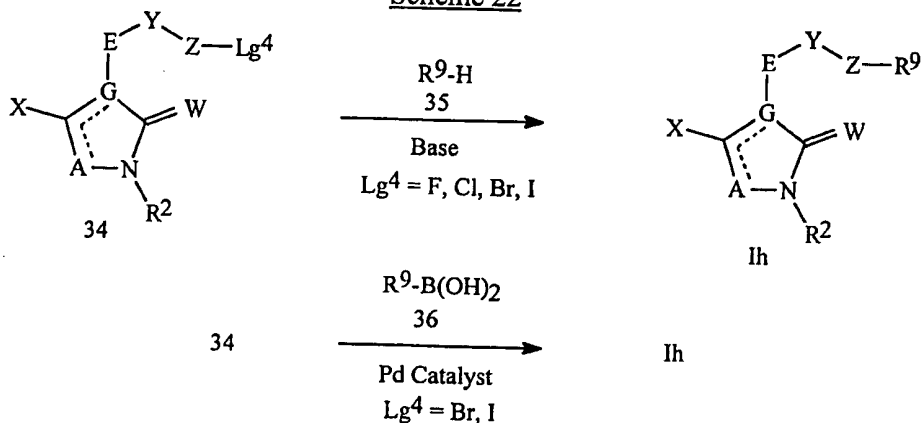
As shown in Scheme 21, compounds of Formula I can be prepared by reacting electrophiles of Formula 33 with anions of Formula 32 (generated by reacting compounds of Formula 32 with the appropriate base).

24

Scheme 21

Also, compounds of Formula Ih can be prepared by reacting electrophiles such as those depicted by Formula 34 with nucleophiles such as those generated by reaction of compounds of Formula 35 with the appropriate base as shown in Scheme 22.

Alternatively, compounds of Formula Ih can be prepared by reacting compounds of Formula 34 bearing leaving groups such as bromide or iodide with for example aryl boronic acids of Formula 36 in the presence of a palladium catalyst.

Scheme 22

It is recognized that some reagents and reaction conditions described above for preparing compounds of Formula I may not be compatible with certain functionalities present in the intermediates. In these instances, the incorporation of

protection/deprotection sequences or functional group interconversions into the synthesis will aid in obtaining the desired products. The use and choice of the protecting groups will be apparent to one skilled in chemical synthesis (see, for example, Greene, T. W.; Wuts, P. G. M. *Protective Groups in Organic Synthesis*, 2nd ed.; Wiley: New York, 1991). One skilled in the art will recognize that, in some cases, after the introduction of a given reagent as it is depicted in any individual scheme, it may be necessary to perform additional routine synthetic steps not described in detail to complete the synthesis of compounds of Formula I. One skilled in the art will also

recognize that it may be necessary to perform a combination of the steps illustrated in the above schemes in an order other than that implied by the particular sequence presented to prepare the compounds of Formula I.

One skilled in the art will also recognize that compounds of Formula I and the
5 intermediates described herein can be subjected to various electrophilic, nucleophilic, radical, organometallic, oxidation, and reduction reactions to add substituents or modify existing substituents.

Without further elaboration, it is believed that one skilled in the art using the preceding description can utilize the present invention to its fullest extent. The
10 following Examples are, therefore, to be construed as merely illustrative, and not limiting of the disclosure in any way whatsoever. Percentages are by weight except for chromatographic solvent mixtures or where otherwise indicated. Parts and percentages for chromatographic solvent mixtures are by volume unless otherwise indicated.
¹H NMR spectra are reported in ppm downfield from tetramethylsilane; s = singlet,
15 d = doublet, t = triplet, m = multiplet and br s = broad singlet. J values indicate coupling constants and are reported in Hz.

EXAMPLE 1

Step A: Preparation of *N*-(2-methoxyphenyl)-2,2-dimethylhydrazinecarboxamide

To a stirred solution of 15.0 g of 2-methoxyphenyl isocyanate in 100 mL of
20 toluene at 5 °C under nitrogen was slowly added 7.65 mL of 1,1-dimethylhydrazine in 10 mL toluene. The cooling bath was then removed and the reaction was allowed to stir for an additional 10 min, and was then concentrated under reduced pressure. The resulting material was dissolved in diethyl ether and concentrated again. A solid was obtained which was triturated with hexanes to afford 21 g of the title compound of
25 Step A as a white solid. ¹H NMR (CDCl₃) δ 8.6 (br s, 1H), 8.24 (m, 1H), 6.95 (m, 2H), 6.85 (m, 1H), 5.35 (br s, 1H), 3.89 (s, 3H), 2.60 (s, 6H).

Step B: Preparation of 5-chloro-2,4-dihydro-4-(2-methoxyphenyl)-2-methyl-3H-1,2,4-triazol-3-one

To a stirred solution of 21 g of the title compound of Step A in 800 mL of
30 dichloromethane under nitrogen was added 29.85 g of triphosgene. The reaction was heated to reflux and allowed to reflux overnight, cooled, and then concentrated under reduced pressure. The resulting residue was dissolved in ethyl acetate, washed with distilled water, and then with saturated aqueous sodium chloride solution. The organic layer was dried (MgSO₄), filtered, and concentrated under reduced pressure. The solid
35 was recrystallized from dichloromethane and the resulting solid was triturated with diethyl ether to afford 10 g of the title compound of Step B as a white solid melting at 152-154 °C. ¹H NMR (CDCl₃) δ 7.45 (t, 1H), 7.25 (d, 1H), 7.05 (m, 2H), 3.84 (s, 3H), 3.53 (s, 3H).

Step C: Preparation of 5-chloro-2,4-dihydro-4-(2-hydroxyphenyl)-2-methyl-3H-1,2,4-triazol-3-one

The title compound of Step B (7.7 g) was dissolved in 65 mL of dichloromethane under nitrogen, cooled to -78 °C, and 34 mL of a 1.0 M boron tribromide solution in dichloromethane was then added over 0.5 h with stirring. After the addition, the cooling bath (dry ice/acetone) was kept in place for an additional 0.5 h and then the reaction was allowed to warm to room temperature. Ice was added to the reaction mixture which was then diluted with diethyl ether and the product was extracted using 1N aqueous sodium hydroxide solution. The aqueous layer was acidified with 6N aqueous hydrochloric acid solution and extracted with dichloromethane and then with ethyl acetate. The organic layers were combined, dried (MgSO₄), filtered and concentrated under reduced pressure. The resulting residue was triturated with diethyl ether to afford 5.54 g of the title compound of Step C as a white solid. ¹H NMR (CDCl₃) δ 8.18 (s,1H), 7.11 (t,2H), 6.91 (t,1H), 6.76 (d,1H), 3.56 (s,3H).

Step D: Preparation of 2,4-dihydro-4-(2-hydroxyphenyl)-5-methoxy-2-methyl-3H-1,2,4-triazol-3-one

To a stirred solution of 5.54 g of the title compound of Step C in 50 mL of methanol and 25 mL of 1,2-dimethoxyethane under nitrogen was added 18.6 mL of 30% sodium methoxide solution in methanol. The reaction was heated at reflux for 5.5 h and then cooled to room temperature. The mixture was diluted with diethyl ether and the product was extracted using 1N aqueous sodium hydroxide solution. The aqueous layer was acidified with 6N aqueous hydrochloric acid solution and extracted with dichloromethane. The organic layer was dried (MgSO₄), filtered, and then concentrated under reduced pressure. The resulting residue was triturated with diethyl ether to afford 3.85 g of the title compound of Step D as a white solid (85% pure). ¹H NMR (CDCl₃) δ 8.40 (br s,1H), 7.20 (m,2H), 7.03 (d,1H), 6.94 (t,1H), 4.00 (s,3H), 3.48 (s,3H).

Step E: Preparation of 4-[2-[(6-chloro-4-pyrimidinyl)oxy]phenyl]-2,4-dihydro-5-methoxy-2-methyl-3H-1,2,4-triazol-3-one

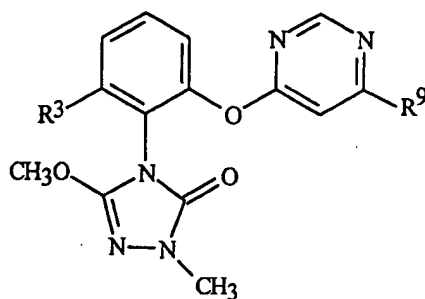
15 g of the intermediate from Step D above were added to a stirred suspension of potassium carbonate (10.3g) in 150 mL of acetonitrile at room temperature. The suspension stirred at room temperature for 1 h. Then 11.1 g of 4,6-dichloropyrimidine were added at room temperature and the reaction was allowed to stir at room temperature for 16 h. The solvent was then removed under reduced pressure and the crude residue was taken up in 150 mL of water. The resulting solids were then filtered, triturated twice with water and suction-dried overnight to yield 19.1g of the desired intermediate. NMR(CDCl₃; 300MHz): δ 3.36 (s,3H), 3.80 (s,3H),

6.93 (d,1H,J=0.9Hz), 7.13 (d,1H,J=8.2Hz), 7.29 (m,1H), 7.45 (m,1H), 8.58 (d,1H, J=7Hz).

Step F: Preparation of 2,4-dihydro-5-methoxy-2-methyl-4-[2-[[6-(2,4,6-trifluorophenoxy)-4-pyrimidinyl]oxy]phenyl]-3H-1,2,4-triazol-3-one

5 0.34 g 2,4,6-trifluorophenol were added to a stirred suspension of potassium carbonate (0.13 g) in 25 mL acetonitrile at room temperature. The resulting suspension was stirred at room temperature for 1 h. Then 0.5 g of the intermediate from Step E were added and the reaction was heated at reflux overnight. The reaction was cooled to room temperature and the solvent was removed under reduced pressure. The crude
10 residue was then purified via column chromatography (1:1/hexanes:ethyl acetate as eluent) to yield 0.34 g of the desired product. NMR(CDCl₃; 300MHz): δ 3.37 (s,3H), 3.77 (s,3H), 6.57 (d,1H, J=0.8Hz), 6.77-6.84 (m,2H), 7.35-7.55 (m,4H), 8.36 (d,1H,J=0.8Hz).

By the procedures described herein together with methods known in the art, the
15 following compounds of Tables 1 to 18 can be prepared. The following abbreviations are used in the Tables which follow: Me = methyl, F = fluorine, Cl = chlorine, Br = bromine, I = iodine, NO₂ = nitro, CN = cyano, Ph = phenyl and PhO = phenoxy.



Structure for Tables 1-4

Table 1

R³ = H

R⁹

2,3-diF-PhO	2,4-diF-PhO	2,5-diF-PhO	2,6-diF-PhO	2,3-diCl-PhO
2,5-diCl-PhO	2,6-diCl-PhO	2,3-diMe-PhO	2,4-diMe-PhO	2,5-diMe-PhO
2,6-diMe-PhO	2,3-diBr-PhO	2,4-diBr-PhO	2,5-diBr-PhO	2,6-diBr-PhO
2,3-diNO ₂ -PhO	2,4-diNO ₂ -PhO	2,5-diNO ₂ -PhO	2,6-diNO ₂ -PhO	3,5-diF-PhO
3,5-diCl-PhO	3,5-diBr-PhO	3,5-diNO ₂ -PhO	3,5-diMe-PhO	

Table 2

 $R^3 = CH_3$ R^9

2,3-diF-PhO	2,4-diF-PhO	2,5-diF-PhO	2,6-diF-PhO	2,3-diCl-PhO
2,4-diCl-PhO	2,5-diCl-PhO	2,6-diCl-PhO	2,3-diMe-PhO	2,4-diMe-PhO
2,5-diMe-PhO	2,6-diMe-PhO	2,3-diBr-PhO	2,4-diBr-PhO	2,5-diBr-PhO
2,6-diBr-PhO	2,3-diNO ₂ -PhO	2,4-diNO ₂ -PhO	2,5-diNO ₂ -PhO	2,6-diNO ₂ -PhO
3,5-diF-PhO	3,5-diCl-PhO	3,5-diBr-PhO	3,5-diNO ₂ -PhO	3,5-diMe-PhO

Table 3

 $R^3 = H$ R^9

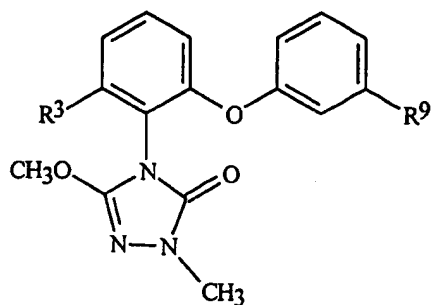
2,3,4-triF-PhO	2,3,5-triF-PhO	2,3,6-triF-PhO	2,4,5-triF-PhO
2,4,6-triF-PhO	2,3,4-triCl-PhO	2,3,5-triCl-PhO	2,3,6-triCl-PhO
2,4,5-triCl-PhO	2,4,6-triCl-PhO	2,3,4-triBr-PhO	2,3,5-triBr-PhO
2,3,6-triBr-PhO	2,4,5-triBr-PhO	2,4,6-triBr-PhO	2,3,4-triMe-PhO
2,3,5-triMe-PhO	2,3,6-triMe-PhO	2,4,5-triMe-PhO	2,4,6-triMe-PhO
2,6-diF-4-NO ₂ -PhO	2,6-diF-4-CN-PhO	2,6-diF-4-Me-PhO	2,6-diF-4-HC≡C-PhO
2,6-diF-4-Br-PhO	2,6-diF-4-Cl-PhO	2,6-diF-4-I-PhO	2,6-diCl-4-Br-PhO
2,6-diCl-4-CN-PhO	2,6-diCl-4-HC≡C-PhO	2,6-diCl-4-NO ₂ -PhO	2,6-diCl-4-I-PhO
2,6-diBr-4-CN-PhO	2,6-diBr-4-HC≡C-PhO	2,6-diBr-4-NO ₂ -PhO	2,6-diBr-4-I-PhO
2,6-diBr-4-Me-PhO	2,6-diMe-4-CN-PhO	2,6-diMe-4-HC≡C-PhO	2,6-diMe-4-NO ₂ -PhO
2,6-diMe-4-I-PhO	2,6-diMe-4-F-PhO	2,6-diMe-4-Cl-PhO	2,6-diMe-4-Br-PhO
2,4-diF-6-Me-PhO	2-Br-6-F-4-Me-PhO	2-Br-6-CN-4-F-PhO	2-Br-4-F-6-Me-PhO
2,4-diF-6-I-PhO	2,4-diF-6-CN-PhO	2,4-diF-6-NO ₂ -PhO	2,4-diF-6-HC≡C-PhO
2,4-diF-6-Br-PhO	2,3,5,6-tetraF-PhO	2,3,4,5-tetraF-PhO	2,3,4,5,6-pentaF-PhO

Table 4

 $R^3 = CH_3$ R^9

2,3,4-triF-PhO	2,3,5-triF-PhO	2,3,6-triF-PhO	2,4,5-triF-PhO
2,4,6-triF-PhO	2,3,4-triCl-PhO	2,3,5-triCl-PhO	2,3,6-triCl-PhO
2,4,5-triCl-PhO	2,4,6-triCl-PhO	2,3,4-triBr-PhO	2,3,5-triBr-PhO
2,3,6-triBr-PhO	2,4,5-triBr-PhO	2,4,6-triBr-PhO	2,3,4-triMe-PhO
2,3,5-triMe-PhO	2,3,6-triMe-PhO	2,4,5-triMe-PhO	2,4,6-triMe-PhO
2,6-diF-4-NO ₂ -PhO	2,6-diF-4-CN-PhO	2,6-diF-4-Me-PhO	2,6-diF-4-HC≡C-PhO
2,6-diF-4-Br-PhO	2,6-diF-4-Cl-PhO	2,6-diF-4-I-PhO	2,6-diCl-4-Br-PhO
2,6-diCl-4-CN-PhO	2,6-diCl-4-HC≡C-PhO	2,6-diCl-4-NO ₂ -PhO	2,6-diCl-4-I-PhO

2,6-diBr-4-CN-PhO	2,6-diBr-4-HC≡C-PhO	2,6-diBr-4-NO ₂ -PhO	2,6-diBr-4-I-PhO
2,6-diBr-4-Me-PhO	2,6-diMe-4-CN-PhO	2,6-diMe-4-HC≡C-PhO	2,6-diMe-4-NO ₂ -PhO
2,6-diMe-4-I-PhO	2,6-diMe-4-F-PhO	2,6-diMe-4-Cl-PhO	2,6-diMe-4-Br-PhO
2,4-diF-6-Me-PhO	2-Br-6-F-4-Me-PhO	2-Br-6-CN-4-F-PhO	2-Br-4-F-6-Me-PhO
2,4-diF-6-I-PhO	2,4-diF-6-CN-PhO	2,4-diF-6-NO ₂ -PhO	2,4-diF-6-HC≡C-PhO
2,4-diF-6-Br-PhO	2,3,5,6-tetraF-PhO	2,3,4,5-tetraF-PhO	2,3,4,5,6-pentaF-PhO



Structure for Tables 5-8

Table 5R³ = HR⁹

2,6-diF-PhO	2,3-diCl-PhO	2,4-diCl-PhO	2,6-diCl-PhO	2,3-diMe-PhO
2,4-diMe-PhO	2,3-diBr-PhO	2,4-diBr-PhO	2,5-diBr-PhO	2,6-diBr-PhO
2,3-diNO ₂ -PhO	2,4-diNO ₂ -PhO	2,5-diNO ₂ -PhO	3,5-diF-PhO	3,5-diCl-PhO
3,5-diBr-PhO	3,5-diNO ₂ -PhO	3,5-diMe-PhO		

Table 6R³ = CH₃R⁹

2,3-diF-PhO	2,4-diF-PhO	2,5-diF-PhO	2,3-diCl-PhO	2,4-diCl-PhO
2,5-diCl-PhO	2,6-diCl-PhO	2,3-diMe-PhO	2,4-diMe-PhO	2,5-diMe-PhO
2,6-diMe-PhO	2,3-diBr-PhO	2,4-diBr-PhO	2,5-diBr-PhO	2,6-diBr-PhO
2,3-diNO ₂ -PhO	2,4-diNO ₂ -PhO	2,5-diNO ₂ -PhO	2,6-diNO ₂ -PhO	3,5-diF-PhO
3,5-diCl-PhO	3,5-diBr-PhO	3,5-diNO ₂ -PhO	3,5-diMe-PhO	

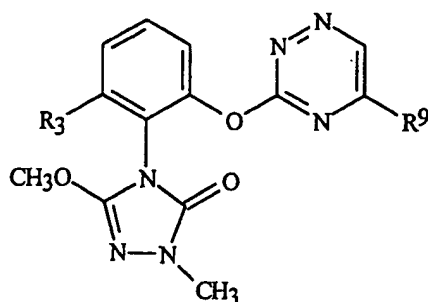
Table 7

$R^3 = H$			
R^9			
2,3,4-triF-PhO	2,3,5-triF-PhO	2,3,6-triF-PhO	2,4,5-triF-PhO
2,4,6-triF-PhO	2,3,4-triCl-PhO	2,3,5-triCl-PhO	2,3,6-triCl-PhO
2,4,5-triCl-PhO	2,4,6-triCl-PhO	2,3,4-triBr-PhO	2,3,5-triBr-PhO
2,3,6-triBr-PhO	2,4,5-triBr-PhO	2,4,6-triBr-PhO	2,3,4-triMe-PhO
2,3,5-triMe-PhO	2,3,6-triMe-PhO	2,4,5-triMe-PhO	2,4,6-triMe-PhO
2,6-diF-4-NO ₂ -PhO	2,6-diF-4-CN-PhO	2,6-diF-4-Me-PhO	2,6-diF-4-HC≡C-PhO
2,6-diF-4-Br-PhO	2,6-diF-4-Cl-PhO	2,6-diF-4-I-PhO	2,6-diCl-4-Br-PhO
2,6-diCl-4-CN-PhO	2,6-diCl-4-HC≡C-PhO	2,6-diCl-4-NO ₂ -PhO	2,6-diCl-4-I-PhO
2,6-diBr-4-CN-PhO	2,6-diBr-4-HC≡C-PhO	2,6-diBr-4-NO ₂ -PhO	2,6-diBr-4-I-PhO
2,6-diBr-4-Me-PhO	2,6-diMe-4-CN-PhO	2,6-diMe-4-HC≡C-PhO	2,6-diMe-4-NO ₂ -PhO
2,6-diMe-4-I-PhO	2,6-diMe-4-F-PhO	2,6-diMe-4-Cl-PhO	2,6-diMe-4-Br-PhO
2,4-diF-6-Me-PhO	2-Br-6-F-4-Me-PhO	2-Br-6-CN-4-F-PhO	2-Br-4-F-6-Me-PhO
2,4-diF-6-I-PhO	2,4-diF-6-CN-PhO	2,4-diF-6-NO ₂ -PhO	2,4-diF-6-HC≡C-PhO
2,4-diF-6-Br-PhO	2,3,5,6-tetraF-PhO	2,3,4,5-tetraF-PhO	2,3,4,5,6-pentaF-PhO

Table 8

$R^3 = CH_3$			
R^9			
2,3,4-triF-PhO	2,3,5-triF-PhO	2,3,6-triF-PhO	2,4,5-triF-PhO
2,4,6-triF-PhO	2,3,4-triCl-PhO	2,3,5-triCl-PhO	2,3,6-triCl-PhO
2,4,5-triCl-PhO	2,4,6-triCl-PhO	2,3,4-triBr-PhO	2,3,5-triBr-PhO
2,3,6-triBr-PhO	2,4,5-triBr-PhO	2,4,6-triBr-PhO	2,3,4-triMe-PhO
2,3,5-triMe-PhO	2,3,6-triMe-PhO	2,4,5-triMe-PhO	2,4,6-triMe-PhO
2,6-diF-4-NO ₂ -PhO	2,6-diF-4-CN-PhO	2,6-diF-4-Me-PhO	2,6-diF-4-HC≡C-PhO
2,6-diF-4-Br-PhO	2,6-diF-4-Cl-PhO	2,6-diF-4-I-PhO	2,6-diCl-4-Br-PhO
2,6-diCl-4-CN-PhO	2,6-diCl-4-HC≡C-PhO	2,6-diCl-4-NO ₂ -PhO	2,6-diCl-4-I-PhO
2,6-diBr-4-CN-PhO	2,6-diBr-4-HC≡C-PhO	2,6-diBr-4-NO ₂ -PhO	2,6-diBr-4-I-PhO
2,6-diBr-4-Me-PhO	2,6-diMe-4-CN-PhO	2,6-diMe-4-HC≡C-PhO	2,6-diMe-4-NO ₂ -PhO
2,6-diMe-4-I-PhO	2,6-diMe-4-F-PhO	2,6-diMe-4-Cl-PhO	2,6-diMe-4-Br-PhO
2-Br-6-F-4-Me-PhO	2-Br-6-CN-4-F-PhO	2-Br-4-F-6-Me-PhO	2,4-diF-6-Me-PhO
2,4-diF-6-CN-PhO	2,4-diF-6-NO ₂ -PhO	2,4-diF-6-HC≡C-PhO	2,4-diF-6-I-PhO
2,4-diF-6-Br-PhO	2,3,5,6-tetraF-PhO	2,3,4,5-tetraF-PhO	2,3,4,5,6-pentaF-PhO

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Structure for Tables 9-12

Table 9R³ = HR⁹

2,3,4-triF-Ph	2,3,5-triF-Ph	2,3,6-triF-Ph	2,4,5-triF-Ph
2,4,6-triF-Ph	2,3,4-triCl-Ph	2,3,5-triCl-Ph	2,3,6-triCl-Ph
2,4,5-triCl-Ph	2,4,6-triCl-Ph	2,3,4-triBr-Ph	2,3,5-triBr-Ph
2,3,6-triBr-Ph	2,4,5-triBr-Ph	2,4,6-triBr-Ph	2,3,4-triMe-Ph
2,3,5-triMe-Ph	2,3,6-triMe-Ph	2,4,5-triMe-Ph	2,4,6-triMe-Ph
2,6-diF-4-NO ₂ -Ph	2,6-diF-4-CN-Ph	2,6-diF-4-Me-Ph	2,6-diF-4-HC≡C-Ph
2,6-diF-4-Br-Ph	2,6-diF-4-Cl-Ph	2,6-diF-4-I-Ph	2,6-diCl-4-Br-Ph
2,6-diCl-4-CN-Ph	2,6-diCl-4-HC≡C-Ph	2,6-diCl-4-NO ₂ -Ph	2,6-diCl-4-I-Ph
2,6-diBr-4-CN-Ph	2,6-diBr-4-HC≡C-Ph	2,6-diBr-4-NO ₂ -Ph	2,6-diBr-4-I-Ph
2,6-diMe-4-Me-Ph	2,6-diMe-4-CN-Ph	2,6-diMe-4-HC≡C-Ph	2,6-diMe-4-NO ₂ -Ph
2,6-diMe-4-I-Ph	2,6-diMe-4-F-Ph	2,6-diMe-4-Cl-Ph	2,6-diMe-4-Br-Ph
2,4-diF-6-Me-Ph	2-Br-6-F-4-Me-Ph	2-Br-6-CN-4-F-Ph	2-Br-4-F-6-Me-Ph
2,4-diF-6-I-Ph	2,4-diF-6-CN-Ph	2,4-diF-6-NO ₂ -Ph	2,4-diF-6-HC≡C-Ph
2,4-diF-6-Br-Ph			

Table 10R³ = CH₃R⁹

2,3,4-triF-Ph	2,3,5-triF-Ph	2,3,6-triF-Ph	2,4,5-triF-Ph
2,4,6-triF-Ph	2,3,4-triCl-Ph	2,3,5-triCl-Ph	2,3,6-triCl-Ph
2,4,5-triCl-Ph	2,4,6-triCl-Ph	2,3,4-triBr-Ph	2,3,5-triBr-Ph
2,3,6-triBr-Ph	2,4,5-triBr-Ph	2,4,6-triBr-Ph	2,3,4-triMe-Ph
2,3,5-triMe-Ph	2,3,6-triMe-Ph	2,4,5-triMe-Ph	2,4,6-triMe-Ph
2,6-diF-4-NO ₂ -Ph	2,6-diF-4-CN-Ph	2,6-diF-4-Me-Ph	2,6-diF-4-HC≡C-Ph
2,6-diF-4-Br-Ph	2,6-diF-4-Cl-Ph	2,6-diF-4-I-Ph	2,6-diCl-4-Br-Ph
2,6-diCl-4-CN-Ph	2,6-diCl-4-HC≡C-Ph	2,6-diCl-4-NO ₂ -Ph	2,6-diCl-4-I-Ph
2,6-diBr-4-CN-Ph	2,6-diBr-4-HC≡C-Ph	2,6-diBr-4-NO ₂ -Ph	2,6-diBr-4-I-Ph

2,6-diBr-4-Me-Ph	2,6-diMe-4-CN-Ph	2,6-diMe-4-HC≡C-Ph	2,6-diMe-4-NO ₂ -Ph
2,6-diMe-4-I-Ph	2,6-diMe-4-F-Ph	2,6-diMe-4-Cl-Ph	2,6-diMe-4-Br-Ph
2,4-diF-6-Me-Ph	2-Br-6-F-4-Me-Ph	2-Br-6-CN-4-F-Ph	2-Br-4-F-6-Me-Ph
2,4-diF-6-I-Ph	2,4-diF-6-CN-Ph	2,4-diF-6-NO ₂ -Ph	2,4-diF-6-HC≡C-Ph
2,4-diF-6-Br-Ph			

Table 11

R³ = HR⁹

2,3,4-triF-PhO	2,3,5-triF-PhO	2,3,6-triF-PhO	2,4,5-triF-PhO
2,4,6-triF-PhO	2,3,4-triCl-PhO	2,3,5-triCl-PhO	2,3,6-triCl-PhO
2,4,5-triCl-PhO	2,4,6-triCl-PhO	2,3,4-triBr-PhO	2,3,5-triBr-PhO
2,3,6-triBr-PhO	2,4,5-triBr-PhO	2,4,6-triBr-PhO	2,3,4-triMe-PhO
2,3,5-triMe-PhO	2,3,6-triMe-PhO	2,4,5-triMe-PhO	2,4,6-triMe-PhO
2,6-diF-4-NO ₂ -PhO	2,6-diF-4-CN-PhO	2,6-diF-4-Me-PhO	2,6-diF-4-HC≡C-PhO
2,6-diF-4-Br-PhO	2,6-diF-4-Cl-PhO	2,6-diF-4-I-PhO	2,6-diCl-4-Br-PhO
2,6-diCl-4-CN-PhO	2,6-diCl-4-HC≡C-PhO	2,6-diCl-4-NO ₂ -PhO	2,6-diCl-4-I-PhO
2,6-diBr-4-CN-PhO	2,6-diBr-4-HC≡C-PhO	2,6-diBr-4-NO ₂ -PhO	2,6-diBr-4-I-PhO
2,6-diBr-4-Me-PhO	2,6-diMe-4-CN-PhO	2,6-diMe-4-HC≡C-PhO	2,6-diMe-4-NO ₂ -PhO
2,6-diMe-4-I-PhO	2,6-diMe-4-F-PhO	2,6-diMe-4-Cl-PhO	2,6-diMe-4-Br-PhO
2,4-diF-6-Me-PhO	2-Br-6-F-4-Me-PhO	2-Br-6-CN-4-F-PhO	2-Br-4-F-6-Me-PhO
2,4-diF-6-I-PhO	2,4-diF-6-CN-PhO	2,4-diF-6-NO ₂ -PhO	2,4-diF-6-HC≡C-PhO
2,4-diF-6-Br-PhO	2,3,5,6-tetraF-PhO	2,3,4,5-tetraF-PhO	2,3,4,5,6-pentaF-PhO

Table 12

R³ = CH₃R⁹

2,3,4-triF-PhO	2,3,5-triF-PhO	2,3,6-triF-PhO	2,4,5-triF-PhO
2,4,6-triF-PhO	2,3,4-triCl-PhO	2,3,5-triCl-PhO	2,3,6-triCl-PhO
2,4,5-triCl-PhO	2,4,6-triCl-PhO	2,3,4-triBr-PhO	2,3,5-triBr-PhO
2,3,6-triBr-PhO	2,4,5-triBr-PhO	2,4,6-triBr-PhO	2,3,4-triMe-PhO
2,3,5-triMe-PhO	2,3,6-triMe-PhO	2,4,5-triMe-PhO	2,4,6-triMe-PhO
2,6-diF-4-NO ₂ -PhO	2,6-diF-4-CN-PhO	2,6-diF-4-Me-PhO	2,6-diF-4-HC≡C-PhO
2,6-diF-4-Br-PhO	2,6-diF-4-Cl-PhO	2,6-diF-4-I-PhO	2,6-diCl-4-Br-PhO
2,6-diCl-4-CN-PhO	2,6-diCl-4-HC≡C-PhO	2,6-diCl-4-NO ₂ -PhO	2,6-diCl-4-I-PhO
2,6-diBr-4-CN-PhO	2,6-diBr-4-HC≡C-PhO	2,6-diBr-4-NO ₂ -PhO	2,6-diBr-4-I-PhO
2,6-diBr-4-Me-PhO	2,6-diMe-4-CN-PhO	2,6-diMe-4-HC≡C-PhO	2,6-diMe-4-NO ₂ -PhO
2,6-diMe-4-I-PhO	2,6-diMe-4-F-PhO	2,6-diMe-4-Cl-PhO	2,6-diMe-4-Br-PhO

2,4-diF-6-Me-PhO

2,4-diF-6-I-PhO

2,4-diF-6-Br-PhO

2-Br-6-F-4-Me-PhO

2,4-diF-6-CN-PhO

2,3,5,6-tetraF-PhO

2-Br-6-CN-4-F-PhO

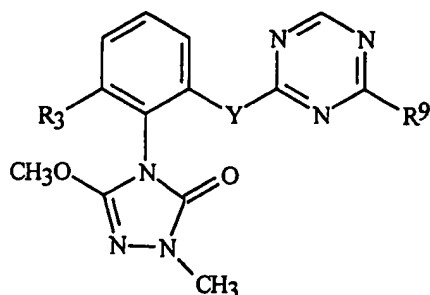
2,4-diF-6-NO₂-PhO

2,3,4,5-tetraF-PhO

2-Br-4-F-6-Me-PhO

2,4-diF-6-HC≡C-PhO

2,3,4,5,6-pentaF-PhO



Structure for Tables 13-18

Table 13

Y = -O-, R³ = HR⁹

2,3,4-triF-Ph	2,3,5-triF-Ph	2,3,6-triF-Ph	2,4,5-triF-Ph
2,4,6-triF-Ph	2,3,4-triCl-Ph	2,3,5-triCl-Ph	2,3,6-triCl-Ph
2,4,5-triCl-Ph	2,4,6-triCl-Ph	2,3,4-triBr-Ph	2,3,5-triBr-Ph
2,3,6-triBr-Ph	2,4,5-triBr-Ph	2,4,6-triBr-Ph	2,3,4-triMe-Ph
2,3,5-triMe-Ph	2,3,6-triMe-Ph	2,4,5-triMe-Ph	2,4,6-triMe-Ph
2,6-diF-4-NO ₂ -Ph	2,6-diF-4-CN-Ph	2,6-diF-4-Me-Ph	2,6-diF-4-HC≡C-Ph
2,6-diF-4-Br-Ph	2,6-diF-4-Cl-Ph	2,6-diF-4-I-Ph	2,6-diCl-4-Br-Ph
2,6-diCl-4-CN-Ph	2,6-diCl-4-HC≡C-Ph	2,6-diCl-4-NO ₂ -Ph	2,6-diCl-4-I-Ph
2,6-diBr-4-CN-Ph	2,6-diBr-4-HC≡C-Ph	2,6-diBr-4-NO ₂ -Ph	2,6-diBr-4-I-Ph
2,6-diBr-4-Me-Ph	2,6-diMe-4-CN-Ph	2,6-diMe-4-HC≡C-Ph	2,6-diMe-4-NO ₂ -Ph
2,6-diMe-4-I-Ph	2,6-diMe-4-F-Ph	2,6-diMe-4-Cl-Ph	2,6-diMe-4-Br-Ph
2,4-diF-6-Me-Ph	2-Br-6-F-4-Me-Ph	2-Br-6-CN-4-F-Ph	2-Br-4-F-6-Me-Ph
2,4-diF-6-I-Ph	2,4-diF-6-CN-Ph	2,4-diF-6-NO ₂ -Ph	2,4-diF-6-HC≡C-Ph
2,4-diF-6-Br-Ph			

Table 14

Y = -CH₂S-, R³ = HR⁹

2,3,4-triF-Ph	2,3,5-triF-Ph	2,3,6-triF-Ph	2,4,5-triF-Ph
2,4,6-triF-Ph	2,3,4-triCl-Ph	2,3,5-triCl-Ph	2,3,6-triCl-Ph
2,4,5-triCl-Ph	2,4,6-triCl-Ph	2,3,4-triBr-Ph	2,3,5-triBr-Ph
2,3,6-triBr-Ph	2,4,5-triBr-Ph	2,4,6-triBr-Ph	2,3,4-triMe-Ph
2,3,5-triMe-Ph	2,3,6-triMe-Ph	2,4,5-triMe-Ph	2,4,6-triMe-Ph

2,6-diF-4-NO ₂ -Ph	2,6-diF-4-CN-Ph	2,6-diF-4-Me-Ph	2,6-diF-4-HC≡C-Ph
2,6-diF-4-Br-Ph	2,6-diF-4-Cl-Ph	2,6-diF-4-I-Ph	2,6-diCl-4-Br-Ph
2,6-diCl-4-CN-Ph	2,6-diCl-4-HC≡C-Ph	2,6-diCl-4-NO ₂ -Ph	2,6-diCl-4-I-Ph
2,6-diBr-4-CN-Ph	2,6-diBr-4-HC≡C-Ph	2,6-diBr-4-NO ₂ -Ph	2,6-diBr-4-I-Ph
2,6-diBr-4-Me-Ph	2,6-diMe-4-CN-Ph	2,6-diMe-4-HC≡C-Ph	2,6-diMe-4-NO ₂ -Ph
2,6-diMe-4-I-Ph	2,6-diMe-4-F-Ph	2,6-diMe-4-Cl-Ph	2,6-diMe-4-Br-Ph
2,4-diF-6-Me-Ph	2-Br-6-F-4-Me-Ph	2-Br-6-CN-4-F-Ph	2-Br-4-F-6-Me-Ph
2,4-diF-6-I-Ph	2,4-diF-6-CN-Ph	2,4-diF-6-NO ₂ -Ph	2,4-diF-6-HC≡C-Ph
2,4-diF-6-Br-Ph			

Table 15

Y = -CH₂S-, R³ = CH₃R⁹

2,3,4-triF-Ph	2,3,5-triF-Ph	2,3,6-triF-Ph	2,4,5-triF-Ph
2,4,6-triF-Ph	2,3,4-triCl-Ph	2,3,5-triCl-Ph	2,3,6-triCl-Ph
2,4,5-triCl-Ph	2,4,6-triCl-Ph	2,3,4-triBr-Ph	2,3,5-triBr-Ph
2,3,6-triBr-Ph	2,4,5-triBr-Ph	2,4,6-triBr-Ph	2,3,4-triMe-Ph
2,3,5-triMe-Ph	2,3,6-triMe-Ph	2,4,5-triMe-Ph	2,4,6-triMe-Ph
2,6-diF-4-NO ₂ -Ph	2,6-diF-4-CN-Ph	2,6-diF-4-Me-Ph	2,6-diF-4-HC≡C-Ph
2,6-diF-4-Br-Ph	2,6-diF-4-Cl-Ph	2,6-diF-4-I-Ph	2,6-diCl-4-Br-Ph
2,6-diCl-4-CN-Ph	2,6-diCl-4-HC≡C-Ph	2,6-diCl-4-NO ₂ -Ph	2,6-diCl-4-I-Ph
2,6-diBr-4-CN-Ph	2,6-diBr-4-HC≡C-Ph	2,6-diBr-4-NO ₂ -Ph	2,6-diBr-4-I-Ph
2,6-diBr-4-Me-Ph	2,6-diMe-4-CN-Ph	2,6-diMe-4-HC≡C-Ph	2,6-diMe-4-NO ₂ -Ph
2,6-diMe-4-I-Ph	2,6-diMe-4-F-Ph	2,6-diMe-4-Cl-Ph	2,6-diMe-4-Br-Ph
2,4-diF-6-Me-Ph	2-Br-6-F-4-Me-Ph	2-Br-6-CN-4-F-Ph	2-Br-4-F-6-Me-Ph
2,4-diF-6-I-Ph	2,4-diF-6-CN-Ph	2,4-diF-6-NO ₂ -Ph	2,4-diF-6-HC≡C-Ph
2,4-diF-6-Br-Ph			

Table 16

Y = -O-, R³ = HR⁹

2,3,4-triF-PhO	2,3,5-triF-PhO	2,3,6-triF-PhO	2,4,5-triF-PhO
2,4,6-triF-PhO	2,3,4-triCl-PhO	2,3,5-triCl-PhO	2,3,6-triCl-PhO
2,4,5-triCl-PhO	2,4,6-triCl-PhO	2,3,4-triBr-PhO	2,3,5-triBr-PhO
2,3,6-triBr-PhO	2,4,5-triBr-PhO	2,4,6-triBr-PhO	2,3,4-triMe-PhO
2,3,5-triMe-PhO	2,3,6-triMe-PhO	2,4,5-triMe-PhO	2,4,6-triMe-PhO
2,6-diF-4-NO ₂ -PhO	2,6-diF-4-CN-PhO	2,6-diF-4-Me-PhO	2,6-diF-4-HC≡C-PhO
2,6-diF-4-Br-PhO	2,6-diF-4-Cl-PhO	2,6-diF-4-I-PhO	2,6-diCl-4-Br-PhO

2,6-diCl-4-CN-PhO	2,6-diCl-4-HC≡C-PhO	2,6-diCl-4-NO ₂ -PhO	2,6-diCl-4-I-PhO
2,6-diBr-4-CN-PhO	2,6-diBr-4-HC≡C-PhO	2,6-diBr-4-NO ₂ -PhO	2,6-diBr-4-I-PhO
2,6-diBr-4-Me-PhO	2,6-diMe-4-CN-PhO	2,6-diMe-4-HC≡C-PhO	2,6-diMe-4-NO ₂ -PhO
2,6-diMe-4-I-PhO	2,6-diMe-4-F-PhO	2,6-diMe-4-Cl-PhO	2,6-diMe-4-Br-PhO
2,4-diF-6-Me-PhO	2-Br-6-F-4-Me-PhO	2-Br-6-CN-4-F-PhO	2-Br-4-F-6-Me-PhO
2,4-diF-6-I-PhO	2,4-diF-6-CN-PhO	2,4-diF-6-NO ₂ -PhO	2,4-diF-6-HC≡C-PhO
2,4-diF-6-Br-PhO	2,3,5,6-tetraF-PhO	2,3,4,5-tetraF-PhO	2,3,4,5,6-pentaF-PhO

Table 17

Y = -CH₂S-, R³ = HR⁹

2,3,4-triF-PhO	2,3,5-triF-PhO	2,3,6-triF-PhO	2,4,5-triF-PhO
2,4,6-triF-PhO	2,3,4-triCl-PhO	2,3,5-triCl-PhO	2,3,6-triCl-PhO
2,4,5-triCl-PhO	2,4,6-triCl-PhO	2,3,4-triBr-PhO	2,3,5-triBr-PhO
2,3,6-triBr-PhO	2,4,5-triBr-PhO	2,4,6-triBr-PhO	2,3,4-triMe-PhO
2,3,5-triMe-PhO	2,3,6-triMe-PhO	2,4,5-triMe-PhO	2,4,6-triMe-PhO
2,6-diF-4-NO ₂ -PhO	2,6-diF-4-CN-PhO	2,6-diF-4-Me-PhO	2,6-diF-4-HC≡C-PhO
2,6-diF-4-Br-PhO	2,6-diF-4-Cl-PhO	2,6-diF-4-I-PhO	2,6-diCl-4-Br-PhO
2,6-diCl-4-CN-PhO	2,6-diCl-4-HC≡C-PhO	2,6-diCl-4-NO ₂ -PhO	2,6-diCl-4-I-PhO
2,6-diBr-4-CN-PhO	2,6-diBr-4-HC≡C-PhO	2,6-diBr-4-NO ₂ -PhO	2,6-diBr-4-I-PhO
2,6-diBr-4-Me-PhO	2,6-diMe-4-CN-PhO	2,6-diMe-4-HC≡C-PhO	2,6-diMe-4-NO ₂ -PhO
2,6-diMe-4-I-PhO	2,6-diMe-4-F-PhO	2,6-diMe-4-Cl-PhO	2,6-diMe-4-Br-PhO
2,4-diF-6-Me-PhO	2-Br-6-F-4-Me-PhO	2-Br-6-CN-4-F-PhO	2-Br-4-F-6-Me-PhO
2,4-diF-6-I-PhO	2,4-diF-6-CN-PhO	2,4-diF-6-NO ₂ -PhO	2,4-diF-6-HC≡C-PhO
2,4-diF-6-Br-PhO	2,3,5,6-tetraF-PhO	2,3,4,5-tetraF-PhO	2,3,4,5,6-pentaF-PhO

Table 18

Y = -CH₂S-, R³ = CH₃R⁹

2,3,4-triF-PhO	2,3,5-triF-PhO	2,3,6-triF-PhO	2,4,5-triF-PhO
2,4,6-triF-PhO	2,3,4-triCl-PhO	2,3,5-triCl-PhO	2,3,6-triCl-PhO
2,4,5-triCl-PhO	2,4,6-triCl-PhO	2,3,4-triBr-PhO	2,3,5-triBr-PhO
2,3,6-triBr-PhO	2,4,5-triBr-PhO	2,4,6-triBr-PhO	2,3,4-triMe-PhO
2,3,5-triMe-PhO	2,3,6-triMe-PhO	2,4,5-triMe-PhO	2,4,6-triMe-PhO
2,6-diF-4-NO ₂ -PhO	2,6-diF-4-CN-PhO	2,6-diF-4-Me-PhO	2,6-diF-4-HC≡C-PhO
2,6-diF-4-Br-PhO	2,6-diF-4-Cl-PhO	2,6-diF-4-I-PhO	2,6-diCl-4-Br-PhO
2,6-diCl-4-CN-PhO	2,6-diCl-4-HC≡C-PhO	2,6-diCl-4-NO ₂ -PhO	2,6-diCl-4-I-PhO
2,6-diBr-4-CN-PhO	2,6-diBr-4-HC≡C-PhO	2,6-diBr-4-NO ₂ -PhO	2,6-diBr-4-I-PhO

2,6-diBr-4-Me-PhO	2,6-diMe-4-CN-PhO	2,6-diMe-4-HC≡C-PhO	2,6-diMe-4-NO ₂ -PhO
2,6-diMe-4-I-PhO	2,6-diMe-4-F-PhO	2,6-diMe-4-Cl-PhO	2,6-diMe-4-Br-PhO
2,4-diF-6-Me-PhO	2-Br-6-F-4-Me-PhO	2-Br-6-CN-4-F-PhO	2-Br-4-F-6-Me-PhO
2,4-diF-6-I-PhO	2,4-diF-6-CN-PhO	2,4-diF-6-NO ₂ -PhO	2,4-diF-6-HC≡C-PhO
2,4-diF-6-Br-PhO	2,3,5,6-tetraF-PhO	2,3,4,5-tetraF-PhO	2,3,4,5,6-pentaF-PhO

Formulation/Utility

Compounds of this invention will generally be used as a formulation or composition with an agriculturally suitable carrier comprising at least one of a liquid diluent, a solid diluent or a surfactant. The formulation or composition ingredients are selected to be consistent with the physical properties of the active ingredient, mode of application and environmental factors such as soil type, moisture and temperature. Useful formulations include liquids such as solutions (including emulsifiable concentrates), suspensions, emulsions (including microemulsions and/or suspoemulsions) and the like which optionally can be thickened into gels. Useful formulations further include solids such as dusts, powders, granules, pellets, tablets, films, and the like which can be water-dispersible ("wetable") or water-soluble. Active ingredient can be (micro)encapsulated and further formed into a suspension or solid formulation; alternatively the entire formulation of active ingredient can be encapsulated (or "overcoated"). Encapsulation can control or delay release of the active ingredient. Sprayable formulations can be extended in suitable media and used at spray volumes from about one to several hundred liters per hectare. High-strength compositions are primarily used as intermediates for further formulation.

The formulations will typically contain effective amounts of active ingredient, diluent and surfactant within the following approximate ranges which add up to 100 percent by weight.

	Weight Percent		
	<u>Active Ingredient</u>	<u>Diluent</u>	<u>Surfactant</u>
Water-Dispersible and Water-soluble Granules, Tablets and Powders.	5-90	0-94	1-15
Suspensions, Emulsions, Solutions (including Emulsifiable Concentrates)	5-50	40-95	0-15
Dusts	1-25	70-99	0-5
Granules and Pellets	0.01-99	5-99.99	0-15
High Strength Compositions	90-99	0-10	0-2

Typical solid diluents are described in Watkins, et al., *Handbook of Insecticide Dust Diluents and Carriers*, 2nd Ed., Dorland Books, Caldwell, New Jersey. Typical liquid diluents are described in Marsden, *Solvents Guide*, 2nd Ed., Interscience, New York, 1950. *McCutcheon's Detergents and Emulsifiers Annual*, Allured Publ. Corp.,
5 Ridgewood, New Jersey, as well as Sisely and Wood, *Encyclopedia of Surface Active Agents*, Chemical Publ. Co., Inc., New York, 1964, list surfactants and recommended uses. All formulations can contain minor amounts of additives to reduce foam, caking, corrosion, microbiological growth and the like, or thickeners to increase viscosity.

Surfactants include, for example, polyethoxylated alcohols, polyethoxylated
10 alkylphenols, polyethoxylated sorbitan fatty acid esters, dialkyl sulfosuccinates, alkyl sulfates, alkylbenzene sulfonates, organosilicones, *N,N*-dialkyltaurates, lignin sulfonates, naphthalene sulfonate formaldehyde condensates, polycarboxylates, and polyoxyethylene/polyoxypropylene block copolymers. Solid diluents include, for example, clays such as bentonite, montmorillonite, attapulgite and kaolin, starch, sugar,
15 silica, talc, diatomaceous earth, urea, calcium carbonate, sodium carbonate and bicarbonate, and sodium sulfate. Liquid diluents include, for example, water, *N,N*-dimethylformamide, dimethyl sulfoxide, *N*-alkylpyrrolidone, ethylene glycol, polypropylene glycol, paraffins, alkylbenzenes, alkyl naphthalenes, oils of olive, castor, linseed, tung, sesame, corn, peanut, cotton-seed, soybean, rape-seed and coconut, fatty
20 acid esters, ketones such as cyclohexanone, 2-heptanone, isophorone and 4-hydroxy-4-methyl-2-pentanone, and alcohols such as methanol, cyclohexanol, decanol and tetrahydrofurfuryl alcohol.

Solutions, including emulsifiable concentrates, can be prepared by simply mixing the ingredients. Dusts and powders can be prepared by blending and, usually, grinding
25 as in a hammer mill or fluid-energy mill. Suspensions are usually prepared by wet-milling; see, for example, U.S. 3,060,084. Granules and pellets can be prepared by spraying the active material upon preformed granular carriers or by agglomeration techniques. See Browning, "Agglomeration", *Chemical Engineering*, December 4, 1967, pp 147-48, *Perry's Chemical Engineer's Handbook*, 4th Ed., McGraw-Hill, New
30 York, 1963, pages 8-57 and following, and WO 91/13546. Pellets can be prepared as described in U.S. 4,172,714. Water-dispersible and water-soluble granules can be prepared as taught in U.S. 4,144,050, U.S. 3,920,442 and DE 3,246,493. Tablets can be prepared as taught in U.S. 5,180,587, U.S. 5,232,701 and U.S. 5,208,030. Films can be prepared as taught in GB 2,095,558 and U.S. 3,299,566.

35 For further information regarding the art of formulation, see U.S. 3,235,361, Col. 6, line 16 through Col. 7, line 19 and Examples 10-41; U.S. 3,309,192, Col. 5, line 43 through Col. 7, line 62 and Examples 8, 12, 15, 39, 41, 52, 53, 58, 132, 138-140, 162-164, 166, 167 and 169-182; U.S. 2,891,855, Col. 3, line 66 through Col. 5, line 17

and Examples 1-4; Klingman, *Weed Control as a Science*, John Wiley and Sons, Inc., New York, 1961, pp 81-96; and Hance et al., *Weed Control Handbook*, 8th Ed., Blackwell Scientific Publications, Oxford, 1989.

- 5 In the following Examples, all percentages are by weight and all formulations are prepared in conventional ways. Compound numbers refer to compounds in Index Tables A-D.

Example A

Wettable Powder

	Compound 8	65.0%
10	dodecylphenol polyethylene glycol ether	2.0%
	sodium ligninsulfonate	4.0%
	sodium silicoaluminate	6.0%
	montmorillonite (calcined)	23.0%.

Example B

Granule

	Compound 9	10.0%
	attapulgate granules (low volatile matter, 0.71/0.30 mm; U.S.S. No. 25-50 sieves)	90.0%.

Example C

Extruded Pellet

	Compound 8	25.0%
	anhydrous sodium sulfate	10.0%
	crude calcium ligninsulfonate	5.0%
	sodium alkyl naphthalenesulfonate	1.0%
25	calcium/magnesium bentonite	59.0%.

Example D

Emulsifiable Concentrate

	Compound 3	20.0%
	blend of oil soluble sulfonates and polyoxyethylene ethers	10.0%
30	isophorone	70.0%.

- The compounds of this invention are useful as plant disease control agents. The present invention therefore further comprises a method for controlling plant diseases caused by fungal plant pathogens comprising applying to the plant or portion thereof to be protected, or to the plant seed or seedling to be protected, an effective amount of a compound of the invention or a fungicidal composition containing said compound. The compounds and compositions of this invention provide control of diseases caused by a broad spectrum of fungal plant pathogens in the Basidiomycete, Ascomycete, Oomycete

- and Deuteromycete classes. They are effective in controlling a broad spectrum of plant diseases, particularly foliar pathogens of ornamental, vegetable, field, cereal, and fruit crops. These pathogens include *Plasmopara viticola*, *Phytophthora infestans*, *Peronospora tabacina*, *Pseudoperonospora cubensis*, *Pythium aphanidermatum*,
 5 *Alternaria brassicae*, *Septoria nodorum*, *Septoria tritici*, *Cercosporidium personatum*, *Cercospora arachidicola*, *Pseudocercospora herpotrichoides*, *Cercospora beticola*, *Botrytis cinerea*, *Monilinia fructicola*, *Pyricularia oryzae*, *Podosphaera leucotricha*, *Venturia inaequalis*, *Erysiphe graminis*, *Uncinula necatur*, *Puccinia recondita*, *Puccinia graminis*, *Hemileia vastatrix*, *Puccinia striiformis*, *Puccinia arachidis*,
 10 *Rhizoctonia solani*, *Sphaerotheca fuliginea*, *Fusarium oxysporum*, *Verticillium dahliae*, *Pythium aphanidermatum*, *Phytophthora megasperma*, *Sclerotinia sclerotiorum*, *Sclerotium rolfsii*, *Erysiphe polygoni*, *Pyrenophora teres*, *Gaeumannomyces graminis*, *Rhynchosporium secalis*, *Fusarium roseum*, *Bremia lactucae* and other genera and species closely related to these pathogens.
- 15 Compounds of this invention can also be mixed with one or more other insecticides, fungicides, nematocides, bactericides, acaricides, growth regulators, chemosterilants, semiochemicals, repellents, attractants, pheromones, feeding stimulants or other biologically active compounds to form a multi-component pesticide giving an even broader spectrum of agricultural protection. Examples of such agricultural
 20 protectants with which compounds of this invention can be formulated are: insecticides such as abamectin, acephate, azinphos-methyl, bifenthrin, buprofezin, carbofuran, chlorfenapyr, chlorpyrifos, chlorpyrifos-methyl, cyfluthrin, beta-cyfluthrin, cyhalothrin, lambda-cyhalothrin, deltamethrin, diafenthiuron, diazinon, diflubenzuron, dimethoate, esfenvalerate, fenoxycarb, fenpropathrin, fenvalerate, fipronil, flucythrinate,
 25 tau-fluvalinate, fonophos, imidacloprid, isofenphos, malathion, metaldehyde, methamidophos, methidathion, methomyl, methoprene, methoxychlor, methyl 7-chloro-2,5-dihydro-2-[[N-(methoxycarbonyl)-N-[4-(trifluoromethoxy)phenyl]amino]carbonyl]indeno[1,2-e][1,3,4]oxadiazine-4a(3H)-carboxylate (DPX-JW062), monocrotophos, oxamyl, parathion, parathion-methyl, permethrin, phorate, phosalone, phosmet, phosphamidon, pirimicarb, profenofos, rotenone, sulprofos, tebufenozide, tefluthrin, terbufos, tetrachlorvinphos, thiodicarb, tralomethrin, trichlorfon and triflumuron; fungicides such as azoxystrobin, benomyl, blastidicin-S, Bordeaux mixture (tribasic copper sulfate), bromuconazole, captafol, captan, carbendazim, carpropamid, chloroneb, chlorothalonil, copper oxychloride,
 30 copper salts, cymoxanil, cyproconazole, cyprodinil (CGA 219417), diclomezine, dicloran, difenoconazole, dimethomorph, diniconazole, diniconazole-M, dodine, edifenphos, epoxiconazole (BAS 480F), famoxadone, fenarimol, fenbuconazole, fenpiclonil, fenpropidin, fenpropimorph, fluazinam, fluquinconazole, flusilazole,

- flutolanil, flutriafol, folpet, fosetyl-aluminum, furalaxyl, hexaconazole, ipconazole, iprobenfos, iprodione, isoprothiolane, kasugamycin, kresoxim-methyl, mancozeb, maneb, mepronil, metalaxyl, metconazole, S-methyl 7-benzothiazolecarbothioate (CGA 245704), myclobutanil, neo-asozin (ferric methanearsonate), oxadixyl,
- 5 penconazole, pencycuron, probenazole, prochloraz, propiconazole, pyrifenoxy, pyroquilon, quinoxifen, spiroxamine (KWG4168), sulfur, tebuconazole, tetraconazole, thiabendazole, thiophanate-methyl, thiram, triadimefon, triadimenol, tricyclazole, triticonazole, validamycin and vinclozolin; nematocides such as aldoxycarb and fenamiphos; bactericides such as streptomycin; acaricides such as amitraz,
- 10 chinomethionat, chlorobenzilate, cyhexatin, dicofol, dienochlor, etoxazole, fenazaquin, fenbutatin oxide, fenpropathrin, fenpyroximate, hexythiazox, propargite, pyridaben and tebufenpyrad; and biological agents such as *Bacillus thuringiensis*, *Bacillus thuringiensis* delta endotoxin, baculovirus, and entomopathogenic bacteria, virus and fungi.
- 15 In certain instances, combinations with other fungicides having a similar spectrum of control but a different mode of action will be particularly advantageous for resistance management. Preferred for better control of plant diseases caused by fungal plant pathogens (e.g., lower use rate or broader spectrum of plant pathogens controlled) or resistance management are mixtures of a compound of this invention with a fungicide
- 20 selected from the group azoxystrobin, benomyl, carbendazim, carpropamid, copper salts, cymoxanil, cyproconazole, cyprodinil, dimethomorph, epoxiconazole, famoxadone, fenpropidin, fenpropimorph, flusilazole, flutolanil, fosetyl-aluminum, kasugamycin, kresoxim-methyl, mancozeb, metalaxyl and oxadixyl, pencycuron, probenazole, propiconazole, pyroquilon, tricyclazole, validamycin. Specifically
- 25 preferred mixtures (compound numbers refer to compounds in Index Tables A-D) are selected from the group: compound 8 and azoxystrobin, compound 8 and benomyl, compound 8 and carbendazim, compound 8 and carpropamid, compound 8 and copper salts, compound 8 and cymoxanil, compound 8 and cyproconazole, compound 8 and cyprodinil, compound 8 and epoxiconazole, compound 8 and famoxadone, compound 8
- 30 and fenpropidin, compound 8 and fenpropimorph, compound 8 and flusilazole, compound 8 and flutolanil, compound 8 and fosetyl-aluminum, compound 8 and kasugamycin, compound 8 and kresoxim-methyl, compound 8 and mancozeb, compound 8 and metalaxyl, compound 8 and oxadixyl, compound 8 and pencycuron, compound 8 and probenazole, compound 8 and propiconazole, compound 8 and
- 35 pyroquilon, compound 8 and tricyclazole, compound 8 and validamycin, compound 9 and azoxystrobin, compound 9 and benomyl, compound 9 and carbendazim, compound 9 and carpropamid, compound 9 and copper salts, compound 9 and cymoxanil, compound 9 and cyproconazole, compound 9 and cyprodinil, compound 9

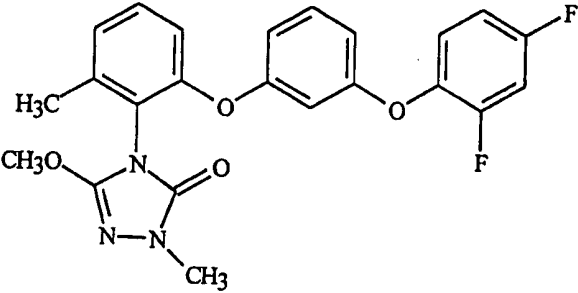
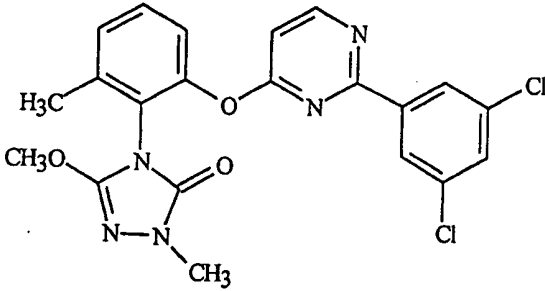
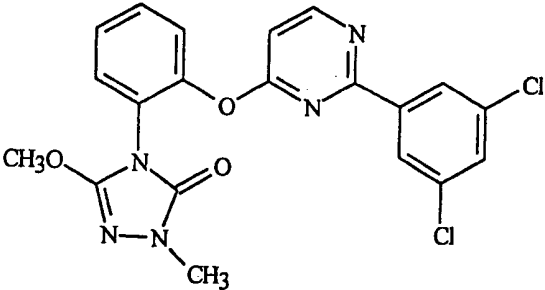
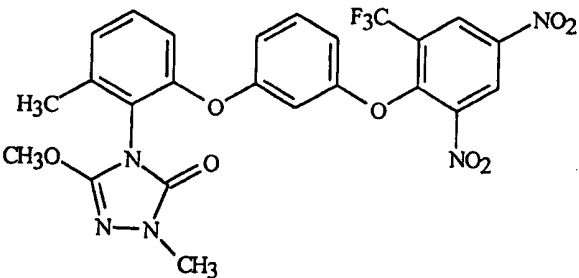
and epoxiconazole, compound 9 and famoxadone, compound 9 and fenpropidin, compound 9 and fenpropimorph, compound 9 and flusilazole, compound 9 and flutolanil, compound 9 and fosetyl-aluminum, compound 9 and kasugamycin, compound 9 and kresoxim-methyl, compound 9 and mancozeb, compound 9 and
5 metalaxyl, compound 9 and oxadixyl, compound 9 and pencycuron, compound 9 and probenazole, compound 9 and propiconazole, compound 9 and pyroquilon, compound 9 and tricyclazole, compound 9 and validamycin, compound 3 and azoxystrobin, compound 3 and benomyl, compound 3 and carbendazim, compound 3 and carpropamid, compound 3 and copper salts, compound 3 and cymoxanil, compound 3
10 and cyproconazole, compound 3 and cyprodinil, compound 3 and epoxiconazole, compound 3 and famoxadone, compound 3 and fenpropidin, compound 3 and fenpropimorph, compound 3 and flusilazole, compound 3 and flutolanil, compound 3 and fosetyl-aluminum, compound 3 and kasugamycin, compound 3 and kresoxim-methyl, compound 3 and mancozeb, compound 3 and metalaxyl, compound 3
15 and oxadixyl, compound 3 and pencycuron, compound 3 and probenazole, compound 3 and propiconazole, compound 3 and pyroquilon, compound 3 and tricyclazole, and compound 3 and validamycin.

Plant disease control is ordinarily accomplished by applying an effective amount of a compound of this invention either pre- or post-infection, to the portion of the plant
20 to be protected such as the roots, stems, foliage, fruit, seeds, tubers or bulbs, or to the media (soil or sand) in which the plants to be protected are growing. The compounds can also be applied to the seed to protect the seed and seedling.

Rates of application for these compounds can be influenced by many factors of the environment and should be determined under actual use conditions. Foliage can
25 normally be protected when treated at a rate of from less than 1 g/ha to 5,000 g/ha of active ingredient. Seed and seedlings can normally be protected when seed is treated at a rate of from 0.1 to 10 g per kilogram of seed.

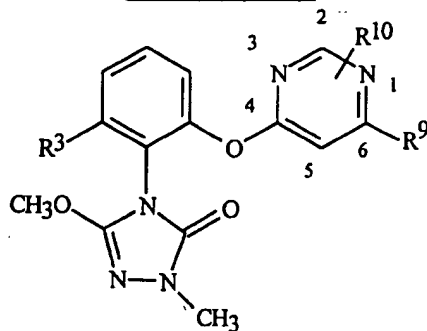
The following TESTS demonstrate the control efficacy of compounds of this invention on specific pathogens. The pathogen control protection afforded by the
30 compounds is not limited, however, to these species. See Index Tables A-E for compound descriptions. The following abbreviations are used in the Index Tables which follow: F = fluorine, Cl = chlorine, Br = bromine, Me = methyl, Et = ethyl, PhO = phenoxy and MeO = methoxy. The abbreviation "Ex. No." stands for "Example Number" and is followed by a number indicating in which example the compound is
35 prepared. The abbreviation "Cmpd No." stands for Compound Number and the abbreviation "mp" stands for melting point.

INDEX TABLE A

<u>Cmpd No.</u>	<u>Structure</u>	<u>mp °C</u>
1		oil*
62		135-137
63		158-160
67		156-158

*See Index Table E for ^1H NMR data.

INDEX TABLE B

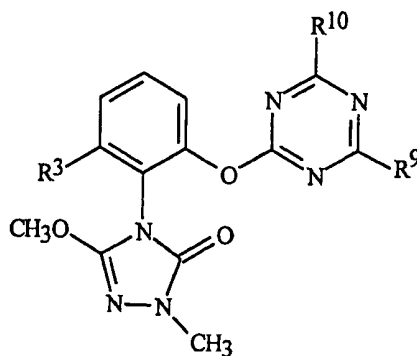


<u>Cmpd No.</u>				
<u>(Ex. No.)</u>	<u>R³</u>	<u>R⁹</u>	<u>R¹⁰</u>	<u>mp °C</u>
3	Me	2,6-diF-PhO	H	164-166
4	Me	2,4-diF-PhO	H	148-149
5	Me	2,3-diF-PhO	H	133-135
6	Me	2,6-diCl-PhO	H	140-143
7	H	2,4-diF-PhO	H	oil*
8 (Ex. 1)	H	2,4,6-triF-PhO	H	125-126
9	Me	2,4,6-triF-PhO	H	178-180
10	H	2,5-diF-PhO	H	oil*
11	Me	2,5-diF-PhO	H	113-115
12	Me	2,6-diMe-PhO	H	122-123
13	Me	2,4,6-triMe-PhO	H	123-124
14	H	2,4,6-triMe-PhO	H	154-156
15	H	2,3,4-triF-PhO	H	120-122
16	Me	2,3,4-triF-PhO	H	98-100
17	H	2,3,5-triF-PhO	H	161-163
18	Me	2,3,5-triF-PhO	H	164-166
19	Me	2,3,6-triF-PhO	H	168-169
20	H	2,4,5-triF-PhO	H	122-124
21	Me	2,4,5-triF-PhO	H	178-180
22	H	2,6-diCl-4-F-PhO	H	212-213
23	H	2,6-diBr-4-F-PhO	H	208-210
24	H	2,3,6-triF-PhO	H	142-144
25	H	2,3,5,6-tetraF-PhO	H	138-140
26	Me	2,3,5,6-tetraF-PhO	H	188-191
27	Me	2,4,6-triF-PhO	5-Me	218-220
28	H	2,4,6-triF-PhO	5-Et	128-130
29	Me	2,4,6-triF-PhO	5-Et	153-154

<u>Cmpd No.</u>	<u>R³</u>	<u>R⁹</u>	<u>R¹⁰</u>	<u>mp °C</u>
30	H	2,4,6-triF-PhO	2-Me	144-145
31	Me	2,6-diF-4-Br-PhO	H	195-198
44	Me	2,4,6-triF-PhO	2-Me	115-118
45	Me	2-Cl-4,6-diF-PhO	H	179-181
46	Me	4-I-2,6-diF-PhO	H	180-184
47	H	2-Cl-4,6-diF-PhO	H	178-179
48	Me	4-Cl-2,6-diF-PhO	H	196
49	H	4-Cl-2,6-diF-PhO	H	165
50	Me	2-I-4,6-diF-PhO	H	132-135
51	Me	2-F-4-Cl-PhO	H	156-157
52	Me	2-Cl-5-Me-PhO	H	139-141
53	Me	2-F-4-Br-PhO	H	150-153
54	Me	2-F-4-Me-PhO	H	136-138
55	Me	3,5-diCF ₃ -PhO	H	133-135
56	Me	2-F-5-CF ₃ -PhO	H	168-171
57	Me	2,4,6-triF-PhO	SMe	158-160
58	Me	2,6-diF-PhCH ₂	H	138-140
59	Me	2-Cl-4-F-PhO	H	144-146
60	Me	2,6-diF-4-(CH ₂ =CH)-PhO	H	130-132

*See Index Table E for ¹H NMR data.

INDEX TABLE C

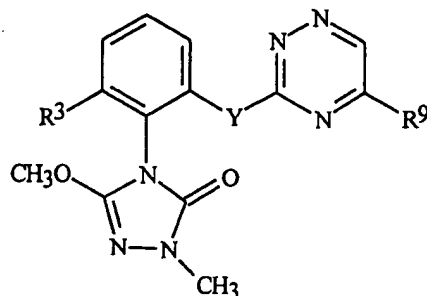


<u>Cmpd No.</u>	<u>R³</u>	<u>R⁹</u>	<u>R¹⁰</u>	<u>mp °C</u>
32	H	3,5-diCl-PhO	MeO	oil*
33	H	2,4-diF-PhO	MeO	50-61
34	H	2,6-diF-PhO	MeO	49-57
35	H	2,6-diCl-PhO	H	49-56

36	H	2,4-diF-PhO	H	52-57
37	H	2,6-diF-PhO	H	163-167
38	CH ₃	2,4-diF-PhO	H	56-61
39	CH ₃	2,6-diF-PhO	H	52-59
40	H	3,5-diCl-Ph	H	214-217
41	CH ₃	3,5-diCl-Ph	H	187-199
42	CH ₃	3,5-diCF ₃ -Ph	H	56-66
43	CH ₃	3-F-4-CH ₃ -Ph	H	188-194

*See Index Table E for ¹H NMR data.

INDEX TABLE D



<u>Cmpd No.</u>	<u>R³</u>	<u>Y</u>	<u>R⁹</u>	<u>mp °C</u>
2	H	O	2,4-diF-Ph	oil*
61	CH ₃	O	3,4-diCl-Ph	oil*
64	H	CH ₂ S	3,4-diMe-Ph	61-72
65	H	CH ₂ S	2,4-diCl-Ph	56-62
66	H	CH ₂ S	2,4-diF-Ph	oil*

*See Index Table E for ¹H NMR data.

INDEX TABLE E

<u>Cmpd. No.</u>	<u>¹H NMR Data (CDCl₃ solution unless indicated otherwise)^a</u>
1	δ 2.26 (s,3H), 3.38 (s,3H), 3.83 (s,3H), 6.6-6.7 (m,3H), 6.8-7.0 (m,3H), 7.0-7.1 (m,2H), 7.2-7.3 (m,2H)
2	δ 3.29 (s,3H), 3.79 (s,3H), 7.01 (m,1H), 7.50 (m,5H), 8.71 (m,1H), 9.59 (s,1H)
7	δ 3.37 (s,3H), 3.78 (s,3H), 6.49 (d,1H, J=0.6), 6.94-7.00 (m,2H), 7.20 (m,1H), 7.30-7.52 (m,4H), 8.38 (s,1H)
10	δ 3.37 (s,3H), 3.78 (s,3H), 6.50 (d,1H, J=0.8), 6.9-7.0 (m,2H), 7.1-7.2 (m,1H), 7.30-7.60 (m,4H), 8.39 (d,1H, J=0.6)

- 32 δ 3.36 (s,3H), 3.87 (s,3H), 3.96 (s,3H), 7.10-7.50 (m,7H)
 61 δ 2.30 (s,3H), 3.30 (s,3H), 3.81 (s,3H), 7.28 (m,2H), 7.45 (t,1H,J=8.0)
 66 δ 3.40 (s,3H), 3.94 (s,3H), 7.02 (m,2H), 7.40 (m,3H), 7.64 (m,1H), 8.22(m,1H),
 9.45 (s,1H)

^a ¹H NMR data are in ppm downfield from tetramethylsilane. Couplings are designated by (s)-singlet, (d)-doublet, (m)-multiplet. J values indicate coupling constants and are reported in Hz.

BIOLOGICAL EXAMPLES OF THE INVENTION

Test compounds were first dissolved in acetone in an amount equal to 3% of the final volume and then suspended at a concentration of 200 ppm in purified water containing 250 ppm of the surfactant Trem® 014 (polyhydric alcohol esters). The resulting test suspensions were then used in the following tests. Spraying these 200 ppm test suspensions to the point of run-off on the test plants is the equivalent of a rate of 500 g/ha.

TEST A

The test suspension was sprayed to the point of run-off on wheat seedlings. The following day the seedlings were inoculated with a spore dust of *Erysiphe graminis* f. sp. *tritici*, (the causal agent of wheat powdery mildew) and incubated in a growth chamber at 20°C for 7 days, after which disease ratings were made.

TEST B

The test suspension was sprayed to the point of run-off on wheat seedlings. The following day the seedlings were inoculated with a spore suspension of *Puccinia recondita* (the causal agent of wheat leaf rust) and incubated in a saturated atmosphere at 20°C for 24 h, and then moved to a growth chamber at 20°C for 6 days, after which disease ratings were made.

TEST C

The test suspension was sprayed to the point of run-off on rice seedlings. The following day the seedlings were inoculated with a spore suspension of *Pyricularia oryzae* (the causal agent of rice blast) and incubated in a saturated atmosphere at 27°C for 24 h, and then moved to a growth chamber at 30°C for 5 days, after which disease ratings were made.

TEST D

The test suspension was sprayed to the point of run-off on tomato seedlings. The following day the seedlings were inoculated with a spore suspension of *Phytophthora infestans* (the causal agent of potato and tomato late blight) and incubated in a saturated atmosphere at 20°C for 24 h, and then moved to a growth chamber at 20°C for 5 days, after which disease ratings were made.

TEST E

- The test suspension was sprayed to the point of run-off on grape seedlings. The following day the seedlings were inoculated with a spore suspension of *Plasmopara viticola* (the causal agent of grape downy mildew) and incubated in a saturated atmosphere at 20°C for 24 h, moved to a growth chamber at 20°C for 6 days, and then incubated in a saturated atmosphere at 20°C for 24 h, after which disease ratings were made.

TEST F

- The test suspension was sprayed to the point of run-off on cucumber seedlings. The following day the seedlings were inoculated with a spore suspension of *Botrytis cinerea* (the causal agent of gray mold on many crops) and incubated in a saturated atmosphere at 20°C for 48 h, and moved to a growth chamber at 20°C for 5 days, after which disease ratings were made.

- Results for Tests A-F are given in Table A. In the table, a rating of 100 indicates 100% disease control and a rating of 0 indicates no disease control (relative to the controls). A dash (-) indicates no test results. ND indicates disease control not determined due to phytotoxicity.

Table A

<u>Cmpd No.</u>	<u>Test A</u>	<u>Test B</u>	<u>Test C</u>	<u>Test D</u>	<u>Test E</u>	<u>Test F</u>
1	100	100	99	100 ^a	100*	0
2	92	99	94	100 ^a	100*	0
3	100	100	86	100 ^a	100*	0
4	99	99	86	0	100*	0
5	-	100	82**	75	100*	0
6	98	100	94	96 ^a	100*	0
7	98	100	91	96 ^a	100*	98
8	100	100	53	100 ^a	95*	0
9	100	100	86	100 ^a	100*	0
10	100	100	32	92	77*	0
11	100	100	86	100 ^a	100*	0
12	98	100	94	97 ^a	100*	0
13	63	100	91	92	100*	0
14	79	99	86	81	97*	0
15	100	99	94	100	59*	10
16	100	100	97	100	100*	0
17	98	100	74	81	11*	70
18	100	100	94	100	100*	0
19	100	100	99	100	100*	0

<u>Cmpd No.</u>	<u>Test A</u>	<u>Test B</u>	<u>Test C</u>	<u>Test D</u>	<u>Test E</u>	<u>Test F</u>
20	98	99	86	100	44*	0
21	100	100	97	100	100*	0
22	99	97	53	97	97*	0
23	77	97	74	-	100*	0
24	100	100	91	76	68*	0
25	99	100	32	0	1*	0
26	99	100	32	100 ^a	100*	0
27	98	97	0	91	-	0
28	92	0	0	57	-	0
29	92	86	0	57	-	0
30	100	100	74	26	13*	0
31	100	100	53	100	100*	0
32	9*	15*	0*	-	42*	-
33	0	85	0	20	4*	0
34	92	93	53	20	0*	0
35	82	86	0	22	13*	0
36	92	94	0	21	7*	0
37	86	97	0	21	7*	0
38	97	97	52	92	1*	0
39	97	94	73	61	1*	0
40	96	99	53	100 ^a	97*	94
41	98	97	53	ND	100*	0
42	100	100	97	85	27*	0
43	86	100	0	ND	100*	69
44	98	100	94	92	100*	0
45	100	100	91	97	100*	0
46	100	100	53	92	100*	0
47	98**	100**	74**	75**	100*	0
48	99	100	94	100	98*	0
49	100	100	94	100	100*	0
50	94	100	99	100	100*	0
51	95	99	99	0	100*	0
52	95	99	94	90	100*	0
53	98	99	94	ND	100*	0
54	95	99	74	0	98*	48
55	100	100	99	96	-	98
57	86	100	91	0	98*	73

<u>Cmpd No.</u>	<u>Test A</u>	<u>Test B</u>	<u>Test C</u>	<u>Test D</u>	<u>Test E</u>	<u>Test F</u>
58	100	99	94	100	88*	0
59	98	99	97	ND	100*	0
60	98	99	86	100	100*	97
61	10*	98*	29*	-	100*	-
62	98	100	99	0	90*	94
63	100	100	91	0	89*	82
64	61	94	74	45	26*	0
65	0	97	0	62	64*	0
66	91	94	74	0	24*	0
67	22	97	53 ^a	56	1*	3

^a Phytotoxicity rating of 20%.

*Tested at 10 ppm.

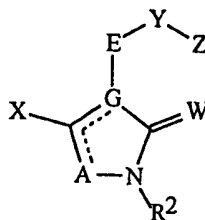
**Tested at 40 ppm.

CLAIMS

What is claimed is:

1. A compound selected from Formula I, *N*-oxides and agriculturally suitable salts thereof,

5



I

wherein

E is 1,2-phenylene optionally substituted with R^3 or both R^3 and R^4 ;

A is O, S, N, NR^5 or CR^6 ;

10 G is C or N; provided that when G is C, then A is O, S or NR^5 and the floating double bond is attached to G; and when G is N, then A is N or CR^6 and the floating double bond is attached to A;

W is O, S, NH, $N(C_1-C_6 \text{ alkyl})$ or $NO(C_1-C_6 \text{ alkyl})$;

X is OR^1 , $S(O)_mR^1$ or halogen;

15 R^1 is C_1-C_6 alkyl, C_1-C_6 haloalkyl, C_2-C_6 alkenyl, C_2-C_6 haloalkenyl, C_2-C_6 alkynyl, C_2-C_6 haloalkynyl, C_3-C_6 cycloalkyl, C_2-C_4 alkylcarbonyl or C_2-C_4 alkoxy carbonyl;

R^2 is H, C_1-C_6 alkyl, C_1-C_6 haloalkyl, C_2-C_6 alkenyl, C_2-C_6 haloalkenyl, C_2-C_6 alkynyl, C_2-C_6 haloalkynyl, C_3-C_6 cycloalkyl, C_2-C_4 alkylcarbonyl, C_2-C_4 alkoxy carbonyl, hydroxy, C_1-C_2 alkoxy or acetyloxy;

20 R^3 and R^4 are each independently halogen, cyano, nitro, hydroxy, C_1-C_6 alkyl, C_1-C_6 haloalkyl, C_2-C_6 alkenyl, C_2-C_6 haloalkenyl, C_2-C_6 alkynyl, C_2-C_6 haloalkynyl, C_1-C_6 alkoxy, C_1-C_6 haloalkoxy, C_2-C_6 alkenyloxy, C_2-C_6 alkynyloxy, C_1-C_6 alkylthio, C_1-C_6 alkylsulfinyl, C_1-C_6 alkylsulfonyl, formyl, C_2-C_6 alkylcarbonyl, C_2-C_6 alkoxy carbonyl, $NH_2C(O)$, $(C_1-C_4 \text{ alkyl})NHC(O)$, $(C_1-C_4 \text{ alkyl})_2NC(O)$, $(R^{13})_3Si$, $(R^{13})_3Ge$, $(R^{13})_3Si-C\equiv C$, phenyl, phenylethynyl, benzoyl or phenylsulfonyl, each phenyl, phenylethynyl, benzoyl and phenylsulfonyl substituted with R^8 and optionally substituted with one or more R^{10} ; or

30 when R^3 and R^4 are attached to adjacent atoms, R^3 and R^4 can be taken together as C_3-C_5 alkylene, C_3-C_5 haloalkylene, C_3-C_5 alkenylene or C_3-C_5 haloalkenylene, each optionally substituted with 1-2 C_1-C_3 alkyl;

- R^5 is H, C₁-C₆ alkyl, C₁-C₆ haloalkyl, C₂-C₆ alkenyl, C₂-C₆ haloalkenyl, C₂-C₆ alkynyl, C₂-C₆ haloalkynyl, C₃-C₆ cycloalkyl, C₂-C₄ alkylcarbonyl or C₂-C₄ alkoxy carbonyl;
- Y is -O-, -S(O)_n-, -NR⁷-, -CH₂O-, -CH₂NR⁷-, -CH₂S(O)_n- or a direct bond; and
 5 the directionality of the Y linkage is defined such that the moiety depicted on the left side of the linkage is bonded to E and the moiety on the right side of the linkage is bonded to Z;
- Z is phenyl, pyrimidinyl or triazinyl, each substituted with R⁹ and optionally substituted with one or more R¹⁰;
- 10 R^6 is H, halogen, C₁-C₆ alkyl, C₁-C₆ haloalkyl, C₂-C₆ alkenyl, C₂-C₆ haloalkenyl, C₂-C₆ alkynyl, C₂-C₆ haloalkynyl or C₃-C₆ cycloalkyl;
- R^7 is H, C₁-C₃ alkyl or C₃-C₆ cycloalkyl; or R^7 is phenyl or benzyl, each optionally substituted on the phenyl ring with halogen, C₁-C₄ alkyl, C₁-C₄ haloalkyl, C₁-C₄ alkoxy, C₁-C₄ haloalkoxy, nitro or cyano;
- 15 R^8 is H, 1-2 halogen, C₁-C₆ alkyl, C₁-C₆ haloalkyl, C₁-C₆ alkoxy, C₁-C₆ haloalkoxy, C₂-C₆ alkenyl, C₂-C₆ haloalkenyl, C₂-C₆ alkynyl, C₁-C₆ alkylthio, C₁-C₆ haloalkylthio, C₁-C₆ alkylsulfinyl, C₁-C₆ alkylsulfonyl, C₃-C₆ cycloalkyl, C₃-C₆ alkenyloxy, CO₂(C₁-C₆ alkyl), NH(C₁-C₆ alkyl), N(C₁-C₆ alkyl)₂, cyano, nitro,
 20 SiR¹⁴R¹⁵R¹⁶ or GeR¹⁴R¹⁵R¹⁶;
- R^9 is phenyl, phenylmethyl, phenoxy, benzoyl, pyridinyl, pyridinyloxy, thienyl, thienyloxy, furanyl, pyrimidinyl or pyrimidinyloxy, each substituted on the aromatic ring with one or more R¹¹ and with one R¹²;
- each R¹⁰ is independently halogen, C₁-C₄ alkyl, C₁-C₄ haloalkyl, C₂-C₄ alkenyl, C₂-C₄ alkynyl, C₁-C₄ alkoxy, nitro or cyano;
- 25 each R¹¹ is independently halogen, cyano, nitro, C₁-C₄ alkyl, C₁-C₄ haloalkyl, C₂-C₆ alkenyl, C₂-C₆ alkynyl, C₁-C₄ alkoxy, C₁-C₄ alkylthio, C₁-C₄ alkylsulfinyl or C₁-C₄ alkylsulfonyl;
- R^{12} is halogen, C₁-C₄ alkyl, C₁-C₄ haloalkyl, C₂-C₆ alkenyl, C₂-C₆ haloalkenyl, C₂-C₆ alkynyl, C₂-C₆ haloalkynyl, C₂-C₆ alkoxyalkyl, C₂-C₆ alkylthioalkyl, C₃-C₆ alkoxyalkynyl, C₇-C₁₀ tetrahydropyranyloxyalkynyl, benzyloxymethyl, C₁-C₄ alkoxy, C₁-C₄ haloalkoxy, C₃-C₆ alkenyloxy, C₃-C₆ haloalkenyloxy, C₃-C₆ alkynyloxy, C₃-C₆ haloalkynyloxy, C₂-C₆ alkoxyalkoxy, C₅-C₉ trialkylsilylalkoxyalkoxy, C₂-C₆ alkylthioalkoxy, C₁-C₄ alkylthio, C₁-C₄ haloalkylthio, C₁-C₄ alkylsulfinyl, C₁-C₄ haloalkylsulfinyl, C₁-C₄ alkylsulfonyl, C₁-C₄ haloalkylsulfonyl, C₃-C₆ alkenylthio, C₃-C₆ haloalkenylthio, C₂-C₆ alkylthioalkylthio, nitro, cyano, thiocyanato, hydroxy, N(R¹³)₂, SF₅, Si(R¹³)₃, Ge(R¹³)₃, (R¹³)₃Si-C≡C-,
 35

- OSi(R¹³)₃, OGe(R¹³)₃, C(=O)R¹⁷, C(=S)R¹⁷, C(=O)OR¹⁷, C(=S)OR¹⁷, C(=O)SR¹⁷, C(=S)SR¹⁷, C(=O)N(R¹⁷)₂, C(=S)N(R¹⁷)₂, OC(=O)R¹⁷, OC(=S)R¹⁷, SC(=O)R¹⁷, SC(=S)R¹⁷, N(R¹⁷)C(=O)R¹⁷, N(R¹⁷)C(=S)R¹⁷, OC(=O)OR¹⁸, OC(=O)SR¹⁸, OC(=O)N(R¹⁷)₂, SC(=O)OR¹⁸, SC(=O)SR¹⁸, S(O)₂OR¹⁷, S(O)₂N(R¹⁷)₂, OS(O)₂R¹⁸ or N(R¹⁷)S(O)₂R¹⁸; or R¹² is phenyl, phenoxy, benzyl, benzyloxy, phenylsulfonyl, phenylethynyl or pyridinylethynyl, each optionally substituted on the aromatic ring with halogen, C₁-C₄ alkyl, C₁-C₄ haloalkyl, C₁-C₄ alkoxy, C₁-C₄ haloalkoxy, nitro or cyano;
- each R¹³ is independently C₁-C₄ alkyl, C₁-C₄ haloalkyl, C₂-C₄ alkenyl, C₁-C₄ alkoxy or phenyl;
- R¹⁴, R¹⁵, and R¹⁶ are each independently C₁-C₆ alkyl, C₂-C₆ alkenyl, C₁-C₄ alkoxy or phenyl;
- each R¹⁷ is independently H, C₁-C₆ alkyl, C₁-C₆ haloalkyl, C₂-C₆ alkenyl, C₂-C₆ haloalkenyl, C₂-C₆ alkynyl, C₂-C₆ haloalkynyl, C₃-C₆ cycloalkyl, phenyl or benzyl, each phenyl and benzyl optionally substituted on the phenyl ring with halogen, C₁-C₄ alkyl, C₁-C₄ haloalkyl, C₁-C₄ alkoxy, C₁-C₄ haloalkoxy, nitro or cyano;
- R¹⁸ is C₁-C₆ alkyl, C₁-C₆ haloalkyl, C₂-C₆ alkenyl, C₂-C₆ haloalkenyl, C₂-C₆ alkynyl, C₂-C₆ haloalkynyl or C₃-C₆ cycloalkyl; or R¹⁸ is phenyl or benzyl, each optionally substituted on the phenyl ring with halogen, C₁-C₄ alkyl, C₁-C₄ haloalkyl, C₁-C₄ alkoxy, C₁-C₄ haloalkoxy, nitro or cyano; and
- m and n are each independently 0, 1 or 2;
- provided that
- i) when E is 1,2-phenylene, A is N, G is N, W is O, X is OMe, R² is CH₃ and Z substituted with R⁹ is
- 6-[3,5-bis(trifluoromethyl)phenyl]-4-pyrimidinyl,
- 6-(2,4-dichlorophenyl)-4-pyrimidinyl,
- 4-[3,5-bis(trifluoromethyl)phenyl]-2-pyrimidinyl,
- 2-[3,5-bis(trifluoromethyl)phenyl]-4-pyrimidinyl,
- 3-[2-(methoxycarbonyl)-6-nitrophenoxy]phenyl,
- 3-(2,6-dicyanophenoxy)phenyl,
- 3-(6-chloro-5-nitro-4-pyrimidinylloxy)phenyl,
- 3-[4-nitro-2-(trifluoromethyl)phenoxy]phenyl,
- 3-(2,6-dimethylphenoxy)phenyl,
- 3-(2-cyano-3-fluorophenoxy)phenyl,
- 3-(2-cyano-6-fluorophenoxy)phenyl, 3-(2,6-dinitrophenoxy)phenyl,

- 3-(2,5-difluorophenoxy)phenyl, 3-(2,5-dimethylphenoxy)phenyl,
 3-(2,5-dichlorophenoxy)phenyl, 3-(3,5-dichlorophenoxy)phenyl,
 3-(2,3-difluorophenoxy)phenyl, 3-(2,4-difluorophenoxy)phenyl,
 3',5'-bis(trifluoromethyl)[1,1'-biphenyl]-3-yl or
 3',5'-dichloro-[1,1'-biphenyl]-3-yl, then Y is other than -O-; and
 ii) when E is 1,2-phenylene, A is N, G is N, W is O, X is OMe, R² is
 CH₃ and Z substituted with R⁹ is
 3-(3,5-dichlorophenyl)-5-methyl-1,2,4-triazin-6-yl, then Y is other
 than -CH₂S-; and
 iii) when A is N, G is N, W is O, X is OMe and EYZ is [2-[[6-[3,5-
 bis(trifluoromethyl)phenyl]-4-pyrimidinyl]oxy]-6-methylphenyl] or
 [2-[3-(2,6-difluorophenoxy)phenoxy]-6-methylphenyl], then R² is
 other than CH₃.
2. A compound of Claim 1 wherein:
 A is O, S or NR⁵;
 G is C;
 R⁹ is phenyl, phenylmethyl, benzoyl, phenoxy, pyridinyl, pyridinyloxy,
 thienyl, thienyloxy, furanyl, pyrimidinyl or pyrimidinylloxy, each
 substituted on the aromatic ring with two or more R¹¹ and with one
 R¹²; and
 R¹² is halogen, C₁-C₄ alkyl, C₁-C₄ haloalkyl, C₁-C₄ alkoxy, C₁-C₄
 haloalkoxy, C₁-C₄ alkylthio, C₁-C₄ haloalkylthio, C₁-C₄
 alkylsulfinyl, C₁-C₄ haloalkylsulfinyl, C₁-C₄ alkylsulfonyl, C₁-C₄
 haloalkylsulfonyl, nitro, cyano, thiocyanato, hydroxy or N(R¹⁷)₂;
 or R¹² is phenyl optionally substituted with halogen, C₁-C₄ alkyl,
 C₁-C₄ haloalkyl, C₁-C₄ alkoxy, C₁-C₄ haloalkoxy, nitro or cyano.
3. A compound of Claim 2 wherein:
 A is O;
 W is O;
 X is OR¹;
 R¹ is CH₃;
 R² is CH₃;
 R³ and R⁴ are each independently halogen or C₁-C₃ alkyl; and
 Y is O, CH₂O or CH₂S(O)_n.
4. The compound of Claim 1 which is selected from the group:
 A is N or CR⁶;
 G is N;

- R^9 is phenyl, phenylmethyl, benzoyl, phenoxy, pyridinyl, pyridinyloxy, thienyl, thienyloxy, furanyl, pyrimidinyl; or pyrimidinyloxy each substituted on the aromatic ring with two or more R^{11} and with one R^{12} ; and
- 5 R^{12} is halogen, C_1 - C_4 alkyl, C_1 - C_4 haloalkyl, C_1 - C_4 alkoxy, C_1 - C_4 haloalkoxy, C_1 - C_4 alkylthio, C_1 - C_4 haloalkylthio, C_1 - C_4 alkylsulfinyl, C_1 - C_4 haloalkylsulfinyl, C_1 - C_4 alkylsulfonyl, C_1 - C_4 haloalkylsulfonyl, nitro, cyano, thiocyanato, hydroxy or $N(R^{17})_2$; or R^{12} is phenyl optionally substituted with halogen, C_1 - C_4 alkyl, C_1 - C_4 haloalkyl, C_1 - C_4 alkoxy, C_1 - C_4 haloalkoxy, nitro or cyano.
- 10
5. The compound of Claim 4 which is selected from the group:
- A is N;
W is O;
X is OR^1 ;
15 R^1 is CH_3 ;
 R^2 is CH_3 ;
 R^3 and R^4 are each independently halogen or C_1 - C_3 alkyl; and
Y is O, CH_2O or $CH_2S(O)_n$.
- 20 6. A fungicidal composition comprising a fungicidally effective amount of a compound of Claim 1 and at least one of a surfactant, a solid diluent or a liquid diluent.
7. A method for controlling plant diseases caused by fungal plant pathogens comprising applying to the plant or portion thereof, or to the plant seed or seedling, a fungicidally effective amount of a compound of Claim 1.

INTERNATIONAL SEARCH REPORT

Intern. Application No

PCT/US 97/17608

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C07D249/12 A01N43/653 C07D403/12 A01N43/66 A01N43/707

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C07D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,Y	WO 95 14009 A (E.I. DU PONT DE NEMOURS AND COMPANY) 26 May 1995 cited in the application see claims 1,2,9,10 ---	1-7
Y	WO 96 17851 A (E.I. DU PONT DE NEMOURS AND COMPANY) 13 June 1996 see claims 1-6,10,11 ---	1-7
P,X	WO 96 36615 A (E.I. DU PONT DE NEMOURS AND COMPANY) 21 November 1996 see claims 1-10 ---	1-7
P,X	WO 96 36616 A (E.I. DU PONT DE NEMOURS AND COMPANY) 21 November 1996 see claims 1,10,11 ---	1,2,6,7
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

G document member of the same patent family

Date of the actual completion of the international search

14 January 1998

Date of mailing of the international search report

30. 01. 98

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Authorized officer

Hartrampf, G

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 97/17608

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 97/17608

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	WO 96 36633 A (E.I. DU PONT DE NEMOURS AND COMPANY) 21 November 1996 see claims 1-8,10,11 ---	1-7
P,X	WO 97 00612 A (E.I. DU PONT DE NEMOURS AND COMPANY) 9 January 1997 cited in the application see claims 6-8,10,12	1-7
P,Y	see compounds no. 313,362,372,378,382,388, 414,419,424,429,443,469-473,498,499,505, 506,543,689,701 -----	1-7

INTERNATIONAL SEARCH REPORT

Information on patent family members

Intern. Application No

PCT/US 97/17608

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